Ultrasonic investigations of linear and star shaped polybutadiene polymers in solutions of cyclohexane, hexane and ethylbenzene

William Bell and Richard A. Pethrick
Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 *Cathedral Street, Glasgow G*1 1*XL, UK*
(*Received* 16 *June* 1981)

Ultrasonic attenuation and velocity measurements are reported on solutions of linear and star shaped polybutadiene in cyclohexane, hexane and ethylbenzene. The linear polymers exhibit viscosity and ultrasonic attenuation characteristics typical of linear polymers. In contrast, the star-shaped polymers exhibit viscosities which are considerably lower than those for the equivalent linear polymer. The ultrasonic attenuation is larger in the star shaped polymers than in the corresponding linear materials and this additional contribution to the attenuation is ascribed to the effects of relaxation of the chemical crosslink. In contrast, the adiabatic compressibilities of the linear and star shaped polymers are essentially independent of molecular weight and structure of the polymer and only a function of the solvent. Analysis of the data presented leads to the conclusion that in this system the excess attenuation is associated with the relaxation of the crosslinks and that the major contribution to such a relaxation comes from entropic rather than volume or enthalpic processes.

Keywords Ultrasonics; polybutadiene; isoentropic compressibility; entanglement; polymer–polymer contacts

INTRODUCTION

Recent ultrasonic investigations of polydimethylsiloxane and its solutions in toluene[1,2] have indicated that for polymers of molecular weight less than that required for entanglement, the ultrasonic attenuation is directly related to the normal mode viscoelastic loss as characterized by the shear relaxation. Increasing the molecular weight leads to a point at which an additional contribution to the observed attenuation is detected and this may be ascribed to the effects of chain entanglement on the normal mode of relaxation[1]. Further increase in the molecular weight leads to a shift of this excess absorption to lower frequencies and a correspondence of the measured shear and acoustic attenuation once more being observed. Dilution of a polymer with molecular weight above that for entanglement, M_c, leads to the observation of a viscosity which does not drop significantly on addition of solvent and an acoustic attenuation which increases markedly with dilution. The increase in the attenuation is consistent with there being a greater number of entanglements in the swollen polymer than in the melt and this is consistent with maintenance of the viscosity whilst effectively reducing the polymer segment density. An earlier investigation of the effects of concentration on the ultrasonic relaxation in solutions of polystyrene in toluene[3] have indicated that up to approximately 10% w/v the acoustic attenuation is simply the sum of segmental and normal mode relaxation contributions. Further increasing the concentration leads to a situation where the acoustic attenuation ceases to be additive and a further contribution is required to explain the observed attenuation characteristics. This additional contribution is assigned to the effects of polymer–polymer contact. Analysis of the acoustic[3] and Raman spectroscopic data[4] indicated that the enthalpy does not change significantly with concentration. Investigation of the adiabatic compressibility allows the magnitude of any additional contribution to the volume relaxation, as a consequence of polymer–polymer contact, to be estimated. In the case of polystyrene in toluene[3], there is a small but finite volume contribution which is, however, insufficient to explain the observed magnitude of the excess attenuation in these systems. The conclusion which emerges is that propagation of a pressure wave leads to entropic fluctuations which give rise to the additional relaxation in this system.

Viscoelastic measurements of dilute solutions of linear and star shaped polybutadiene polymers[5] have indicated that the latter exhibit a relaxation spectrum which is different from that of the linear equivalent. Using a Birnboim–Schrag multiple damped resonator[6] it was possible to show that the linear polymers were uniform to the simple model of Zimm[7] using exact eigen values and a hydrodynamic interaction parameter $h^* = 0.15$. Data on the star polymers were similarly shown to fit the Zimm–Kilb[8,9] theory for branched chain polymers using exact eigen values as 1.13 $h^* = 01$. Good agreement between theory and experiment[5] indicates that interpolation of viscoelastic data in this system is most probably valid. The present investigation is based on the polymers used in the above investigation and was performed on a dilute solution so as to allow the effects of chemical solutions to be differentiated from those of polymer–polymer solutions[2]. Characterization of the acoustic properties of the system might be helpful in the understanding of the

0032–3861/82/030369–05$03.00

Table 1 Characteristic of the polybutadiene

Polymer M_n*	Type
10000	Linear
240000	Linear
215000	Star-shaped
240000	Star-shaped
600000	Linear

* M_n values are obtained from g.p.c. measurements, the data were provided by Dr F. C. Loveless of Uniroyal Oxford Management and Research Centre, Middlebury, Connecticut

critical entanglements produced on increasing the concentration of the solutions of linear polymers.

Experimental materials

The polybutadienes used in this study were very similar to those used in the viscoelastic study described above[5], and were kindly supplied by Drs W. V. Smith and F. C. Loveless of Uniroyal Research Centre. These polymers were synthesized using tert-butyllithium as the catalyst and their microstructure as confirmed by ^{13}C n.m.r. was approximately 55% *trans*, 38% *cis* and 10% vinyl. The four armed star polymers were prepared using tetrafunctional linkage of the arms with dimethylterephthalate[10]. The g.p.c. analysis of the polymers is listed in *Table 1*. The ratio of the weight to number average molecular weights was typically better than 1.1. Although not the identical samples used in the viscoelastic investigations they were prepared by the same workers and were apparently equivalent and identical materials. The solvents used were AnalaR grade where available. The solvents were dried and redistilled before use. The solutions were prepared by shaking the solid and liquid for several days at room temperature. The stock solution so obtained was then diluted to give the required concentrations. Care was taken to avoid the effects of photochemical degradation of the polybutadiene.

Ultrasonic measurements

Attenuation data (α/f^2) were obtained over a frequency range 1–100 MHz using a combination of two techniques described previously[1,2]; acoustic resonator 1–10 MHz and conventional pulse technique 15–100 MHz. The precision was better than 2% over the entire frequency range. Velocity measurements (v) were performed using the acoustic resonator at a nominal frequency of 1.5 MHz and have a precision of 1 part in 10^4.

Density measurements

The densities of the lowest molecular weight polymers and their solutions were determined using an Anton Paar densimeter (DMA 60); the viscous solution and highest molecular weight polymers were measured using specific gravity bottles. In both cases the precision was better than 0.1%.

Viscosity measurements

The steady state flow viscosities of the polymers and their solutions were determined using suspended level viscometers (Poulten and Selfe) thermostatically controlled to ±0.1K and used according to BS188. The precision of the measurements was better than 0.5% for the viscosity determination, a range of calibrated viscometers being used to cover the entire range of viscosities encountered.

RESULTS AND DISCUSSION

The principal objective of this investigation was to ascertain what the effects would be on the ultrasonic propagation of a permanent crosslink within a polymer. Previous studies of linear polymers have indicated that increasing $[\eta]\ c = 10$, where $[\eta]$ is the intrinsic viscosity and c is the concentration, leads to significant polymer–polymer interactions. Whilst it was possible, as discussed above, to deduce that an entanglement increases the acoustic absorption by entropic contributions to the relaxation[2], a direct proof of this statement was lacking.

Viscosity data

The effects of changing the molecular weight, chain structure and solvent are summarized in *Figure 1*. In

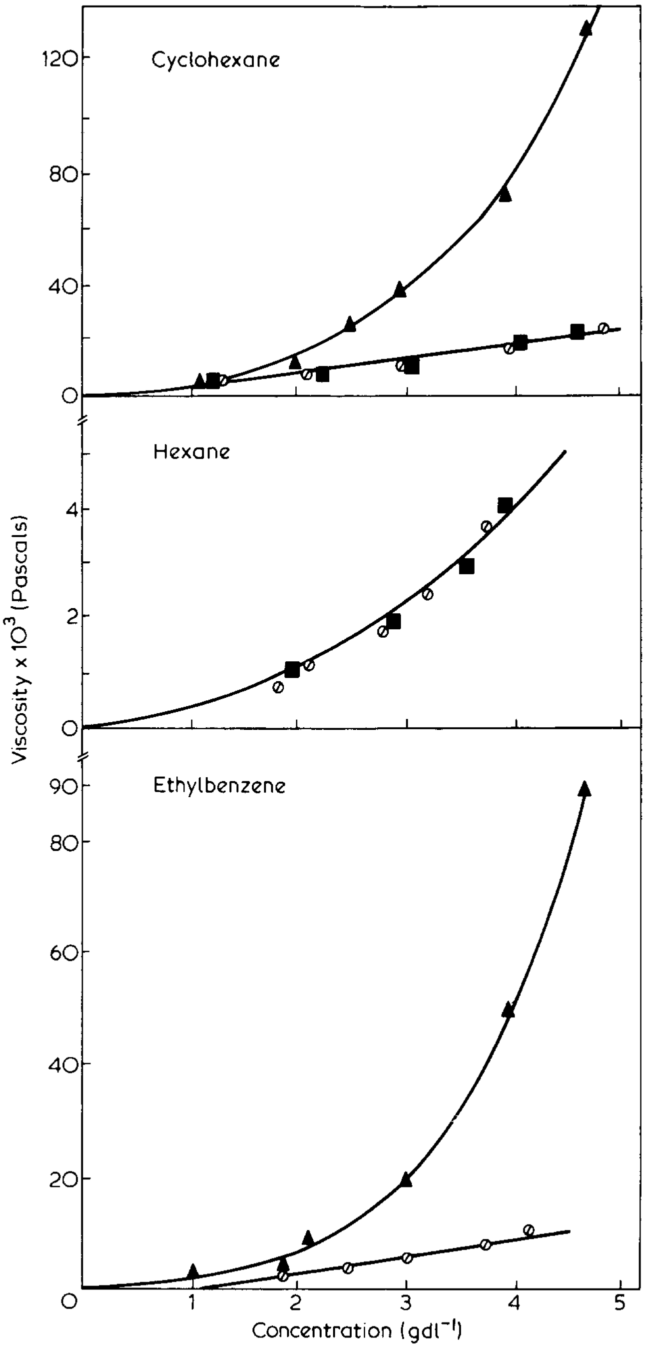

Figure 1 Variation of viscosity with concentration for various solvents. Polybutadiene linear ▲, 240,000; star shaped ■, 215,000 and ⊘, 240,000

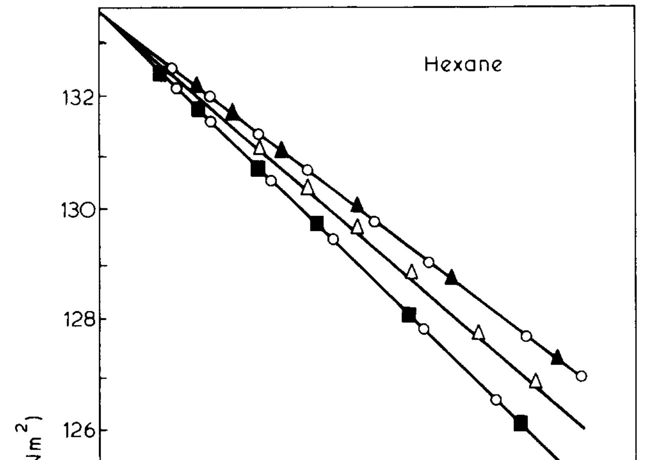

Figure 2 **Adiabatic compressibility variation with concentration for various solvents. Polybutadiene linear ○, 10 000; ▲, 240,000; △, 600 000; star shaped ■, 215 000**

general, the star shaped polymers of an equivalent molecular weight exhibit lower viscosities than their corresponding linear counterparts. Varying the concentration of the polymer indicates that for the star-shaped polymers a linear dependence on the concentration is observed, whereas the linear polymers exhibit a definite curvature in their plots. The critical entanglement molecular weight for polybutadiene is 5600, indicating that the 240000 and 600000 linear materials are above the critical molecular weight for entanglement. The intrinsic viscosity of polybutadiene is 0.55 which indicates that at a concentration of 2g/dl the polymer is in the semi-dilute region and will at 5g/dl enter the semi-concentrated region[11]. However, the concentrations are still insufficient for transient polymer–polymer contact to be observed. The viscosity data would also imply that the star shaped polymers appeared to act as though they were considerably smaller and as such even at a concentration of 5g/dl were only just approaching the semi-dilute viscosity region. Comparison of the behaviour observed in the different solvents indicates that the viscosity is highest in cyclohexane and lowest in hexane, indicative of the extent to which chain expansion occurs in these solvents[12].

Adiabatic compressibility data

Measurements of the velocity of sound propagation as a function of concentration at 303K were found to be approximately linear as were the density variations. Combination of these data using the Laplace equation, adiabatic compressibility, $\kappa = 1/v^2\rho$, yield the data presented in *Figure 2*. In the case of ethylbenzene and cyclohexane there is no dependence of the observed compressibilities with either molecular weight or change from linear to branched chain structure. This observation is consistent with the concept that the compressibility is measuring the local interaction of solvent and polymer and the compressibility of the surrounding solvent. Both these contributions operate at a molecular level and therefore would not be expected to exhibit a molecular weight dependence. Similar observations were made for ethylbenzene, *Figure 2*, and basically the same interpretation applies. However, in the case of hexane there is an apparent molecular weight and structural sensitivity. The low molecular weight linear materials cluster around a single line, the highest molecular weight polymer—600 000, however, exhibits a dependence which is lower than the corresponding linear polymers. Similarly, the star shaped polymers exhibit a dependence which is lower than that of the linear polymers. From the viscosity data it would appear that the thermodynamic quality of the solvent in the case of hexane is different from that in either cyclohexane or ethylbenzene. The strength of the polymer–solvent interaction can be calculated on the basis of the approach described elsewhere[13] and the 'solvation numbers' obtained are presented in *Table 2*. The magnitude of the solvation number reflects the quality of the solvent[12]. The lower compressibility in the case of the 600 000 polymer may therefore be ascribed to intra- and possibly inter-polymer–polymer interactions. Similarly, the non-linearity of the viscosity plots, *Figure 1*, and the decrement in the adiabatic compressibility, *Table 2*, would imply a more interacting situation in hexane than in the other solvents.

Acoustic attenuation

The acoustic attenuation of linear polybutadiene has been reported previously[14]. Unlike many other polymers it does not exhibit a large rotational isomeric contribution and the observed attenuation corresponds closely to that predicted by the Wang and Zimm model[9]. The attenuation in the case of the linear polymers is independent of frequency over the frequency range 1–10 MHz, a relaxation being observed between 10 and 100 MHz ascribed to a combination of normal mode and rotational isomeric processes, both of which have small amplitudes. The attenuation was independent of frequency for all the solutions investigated with the exception of the highest molecular weight linear material, 600 000, and the star shaped polymers. Both exhibited a

Table 2 Solvation values

Polymer	Type of solvent	Cyclo-hexane	Hexane	Ethyl benzene
10 000	Linear	0.27	0.56	0.09
215 000	Star	0.20	0.53	–
240 000	Star	0.27	0.51	0.11
240 000	Linear	0.15	0.45	0.09
600 000	Linear	0.14	0.46	0.12

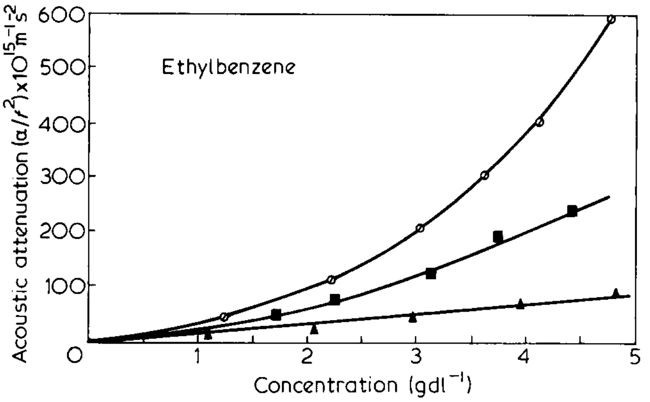

Figure 3 Acoustic attenuation for ethylbenzene solutions of linear and star shaped polybutadienes. Polymer linear ▲, 240 000; star shaped ■, 215 000; ⊘, 240 000

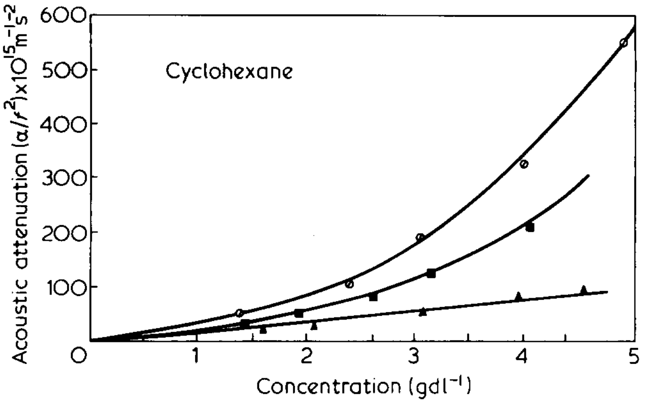

Figure 4 Acoustic attenuation for cyclohexane solutions of linear and star shaped polybutadienes. Polymer linear ▲, 240 000; star shaped ■, 215 000; ⊘, 240 000

frequency dependence in the region 1–10 MHz. The amplitudes of the acoustic attenuation at a nominal frequency of 1 MHz are presented for the various solvents investigated in *Figures 3–5*. The behaviour in cyclohexane and ethylbenzene is very similar, the star shaped polymers exhibiting a non-linear dependence of the attenuation on concentration, whereas the linear polymers exhibit a linear concentration dependence. Using viscosity data, *Figure 1*, and the appropriate viscoelastic model[8], it is possible to calculate the contribution to the observed acoustic attenuation. The method used has been described elsewhere[3]. It was found that the calculated contribution in the case of the low molecular weight polybutadiene polymers was approximately half of the observed attenuation, the residual being ascribed to conformational relaxation. In the case of the star polymers the calculated contribution was only approximately twice that for the equivalent linear polymer, whilst the observed attenuation was approximately three to four times this value. Clearly, the modification in the viscoelastic spectrum as a consequence of the formation of the star is insufficient to explain the observed magnitude of the attenuation. It would therefore appear that the 'excess' attenuation in the case of the star polymers is a direct consequence of the chemical crosslink. Since the adiabatic compressibilities of the linear and star shaped polymers are essentially similar in ethylbenzene and cyclohexane it therefore appears that the increase in the amplitude cannot be attributed to volume relaxation. The viscosities of the star shaped polymers are lower than their equivalent linear polymers. However, the different distribution of the relaxation processes does lead to a larger normal mode contribution in the megahertz work[5]. However, theoretical calculations indicate that this is insufficient to explain the observed effects. The 'excess' in the acoustic attenuation must therefore be ascribed to either an enthalpy or entropy fluctuation. On stereochemical grounds we would not expect the enthalpy difference of the crosslink to be very different from that of the main chain, and therefore the observed increase must be attributed to entropic effects. To establish the relative contributions to the observed excess, the pressure dependence of the acoustic attenuation would be required to be measured. Facilities for this type of measurement do not at present exist at Strathclyde.

In the case of hexane solutions, the excesses are somewhat smaller, indicative of a slightly more extended structure to the polymer[12]. This is consistent with the curvature observed in the concentration dependence of the viscosity. The non-linear and larger observed attenuation in the case of the highest molecular weight linear polybutadiene polymer is consistent with there occurring significant inter- and intra-polymer interactions. In essence, the excess can be assigned to the relaxation of the excluded volume contribution. Calculation of the normal mode contribution for the linear polymer[9] is consistent with the observed increase in the attenuation. The amplitude, however, is rather larger than predicted.

CONCLUSION

The ultrasonic investigation of star and linear polybutadiene polymers in solution in cyclohexane, hexane and ethylbenzene indicates the effects of difference in the molecular weight, chain structure and solvent. The excesses, defined as the difference between the predictions of viscoelastic and segmental relaxation, can be ascribed to polymer–polymer interaction. In the case of the star shaped polymers, the excess is observed well below the point at which polymer–polymer contacts will be anticipated to occur and therefore is a consequence of the entropic fluctuations of the chains involved in the crosslink and results from the applied stresses associated with the propagating sound wave. In the case of the high molecular weight linear polymer, the excess may be ascribed to a combination of inter- and intra-coil contacts, but most probably has the same entropic origins.

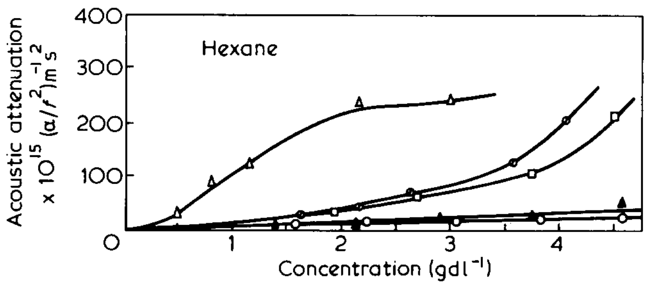

Figure 5 Acoustic attenuation for hexane solutions of linear and star shaped polybutadiene. Polymer linear ○, 10 000; ▲, 240 000; △, 600 000; star shaped □, 215 000; ⊘, 240 000

REFERENCES

1 Bell, W., North, A. M., Pethrick, R. A. and Poh, B. T. *J.C.S. Faraday Trans. II* 1979, **75**, 1115–1127

2 Bell, W., Daly, J., North, A. M., Pethrick, R. A. and Poh, B. T. *J.C.S. Faraday Trans. II* 1979, **75**, 1452–1464

3 Dunbar, J. I., Steinhauer, D. B., North, A. M. and Pethrick, R. A. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 263

4 Speak, R. and Shepard, I. W. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 997

5 Osaki, K., Mitsuda, Y., Johnson, R. M., Schrag, J. L. and Ferry, J. D. *Macromolecules* 1972, **5**, 17

6 Schrag, J. L. and Johnson, R. M. *Rev. Sci. Instrum.* 1971, **42**, 224

7 Zimm, B. H. *J. Chem. Phys.* 1956, **24**, 269

8 Zimm, B. H. and Kilb, R. W. *J. Polym. Sci.* 1959, **37**, 19

9 Wang, F. C. and Zimm, B. H. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 1619

10 Michelin et Cie, Belgium Patent BE-752641-Q

11 Simha, R. and Utracki, L. *J. Polym. Sci.* 1963, **A1**, 1089

12 Yamakawa, H. Modern Theory of Polymer Solutions, Harper and Row, New York (1971)

13 Bell, W. and Pethrick, R. A. *Eur. Polym. J.* 1972, **8**, 927

14 Dunbar, J. H., North, A. M. and Pethrick, R. A. *Polymer* 1977, **18**, 577