

Acoustic and Viscometric Studies of Solutions of Polystyrene and High-Impact Polystyrene in Benzene, Toluene, and Tetrahydrofuran

MUSTAFA M. F. AL-JARRAH, *Petroleum Research Center, Jadiryah P.O. Box 10039, Baghdad*, AMAR H. AL-DUJAILI, *Department of Chemistry, College of Education, Baghdad University*, and SUBHI K. HASSUN, *Department of Physics, College of Education, Baghdad University, Baghdad, Iraq*

Synopsis

Ultrasonic measurements of polystyrene (PS) and high-impact polystyrene (HIPS) solutions in benzene, toluene, and tetrahydrofuran are reported at 2-MHz frequency. Effect of solvent and the rubbery phase of HIPS on the ultrasonic measurements are discussed. Observed relaxation times demonstrate the interaction of polymer-polymer macromolecules and polymer-solvent molecules. Results show a linear increase of velocity, density, viscosity, absorption coefficient, relaxation time, and relaxation amplitude values with increase of PS and HIPS concentrations. In contrast as a result of interaction between polymer molecules and solvent molecules compressibility decreased with increasing polymer concentration.

INTRODUCTION

In recent reports, we have studied the molecular association of polyvinyl chloride (PVC) solution in tetrahydrofuran (THF)¹ and polyethylene oxide aqueous solution,² using ultrasonic technique.

In previous studies we have focused our attention on the molecular association of living polymer solutions in hydrocarbon solvents, using viscometric technique³ and on the association behavior of asphaltenes by viscometric and osmometric technique.⁴

Dynamic properties of polymer solutions is a subject of fundamental and practical interest. The acoustic relaxation of narrow molecular weight PS in dilute solution has indicated⁵ that for the localized modes causing high-frequency absorption in PS entanglement effect were primary entropic in nature. Several interesting features have been observed⁶ when experiments were conducted to determine the effect of chain entanglements of polydimethylsiloxanes on the longitudinal and shear dynamic ultrasonic relaxation processes. Ultrasonic studies of aqueous solutions of polyvinyl alcohol and of sodiumcarboxymethyl dextran⁸ revealed the effect of polymer-polymer interactions and the effect of polymer chains in solutions.

PS and HIPS are of great industrial importance, and their behavior in solution is useful for several applications in both solution and solid state. Previous work on PS was mainly concerned with narrow molecular weight distribution PS, and no reports on industrial grade PS was observed in the literature. Ultrasonic studies of styrene-butadiene-styrene triblok copolymers⁹ provided

TABLE I
Some Characteristics of PS and HIPS

	\overline{M}_n	\overline{M}_w	\overline{M}_v	\overline{M}_z	Q^a	Butadiene content
PS	59,690	379,000	380,800	125,650	6.35	0
HIPS	61,500	419,300	403,500	122,239	6.82	5%

^a The polydispersity that represent molecular weight distribution.

useful observations on the phase behavior of the PS and polybutadiene segment as well as on the solution behavior of their semidilute solution. However, no information is available on the behavior of HIPS in different solvents using ultrasonic technique. HIPS is normally used in applications where its rubbery phase (butadiene) gives the flexibility needed for high-impact applications. HIPS is a copolymer of styrene and butadiene with about 5% butadiene content.

The objective of this work was to ascertain the effect of solvent on the longitudinal (acoustic) chain relaxation processes of industrial grade PS and further to understand the influence of the rubbery phase (butadiene) of HIPS.

EXPERIMENTAL

PS and HIPS samples were obtained from BASF (West Germany) and have the characteristics summarized in Table I. These grades are used by local thermoplastic processors for the production of several plastic articles.

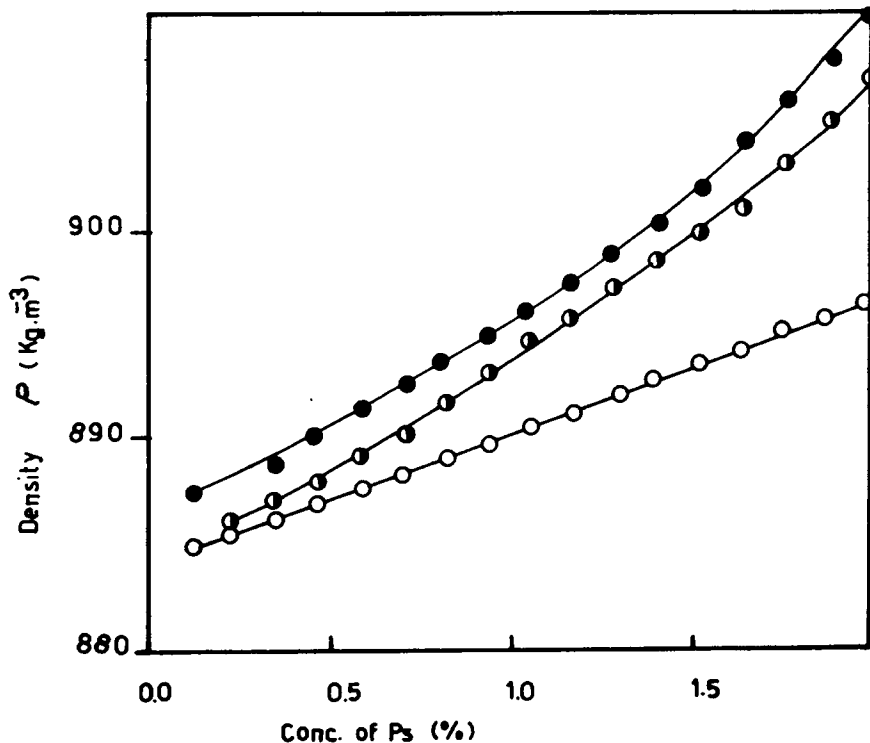


Fig. 1. Linear increase of density with increasing concentration of PS in different solvents: ○ benzene, ◐ toluene, and ● THF.

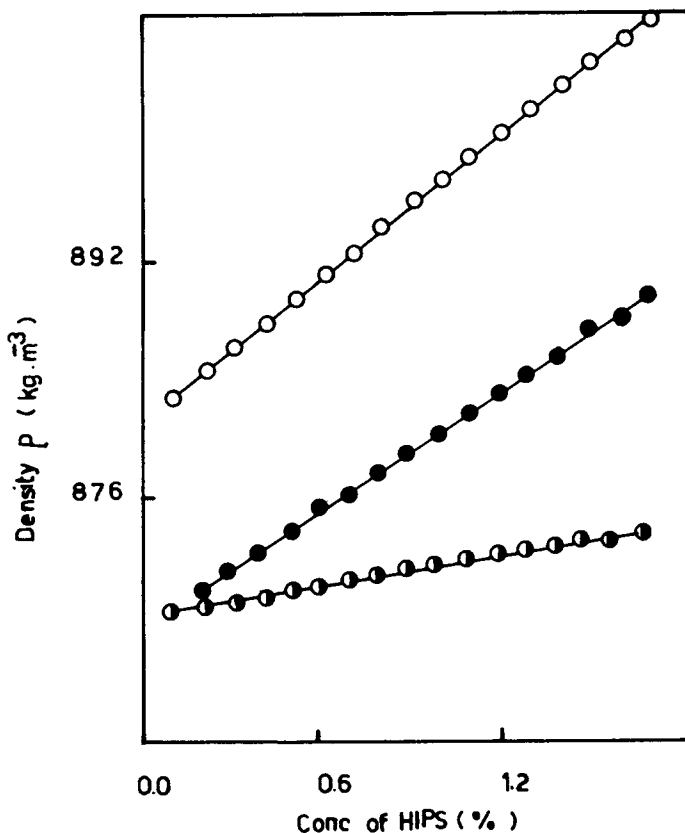


Fig. 2. Linear increase of density with increasing concentration of HIPS in different solvents: ○ benzene, ◐ toluene, and ● THF.

A series of polymer solutions were prepared by adding a known weight of the polymer to a measured weight of the solvents. Solvents (viz. benzene, toluene, and THF) were HPLC grade supplied by Fluka (West Germany) and were dried with calcium hydride and molecular sieves (4A) filtered through micropore filters prior to use.

The viscosity and intrinsic viscosity $[\eta]$ of polymer solution were determined using an Ubbelohd dilution type viscometer. The viscometer was immersed in a bath maintained at a constant temperature (289.15 ± 0.01 K). Density was measured with a pycnometer of 20-mL capacity. The accuracy of the viscosity and density measurements was ± 0.015 and 0.01%, respectively.

Ultrasonic measurements were made with 2-MHz pulse technique of the sender-receiver type, PHWE (West Germany). The metal vibrator was coated with oil and kept in contact with the wall of the glass tank containing the test sample. The receiver quartz crystal was mounted on a vernier scale of slow motion. The receiver crystal could be displaced parallel to the sender through 9 cm. The sender and receiver pulse were displayed on two traces of a cathode ray oscillograph, and the time delay of the received pulse was measured.

The isoentropic compressibility (β) were calculated using the well-known Laplace equation:

$$\beta = [PC^2]^{-1} \quad (1)$$

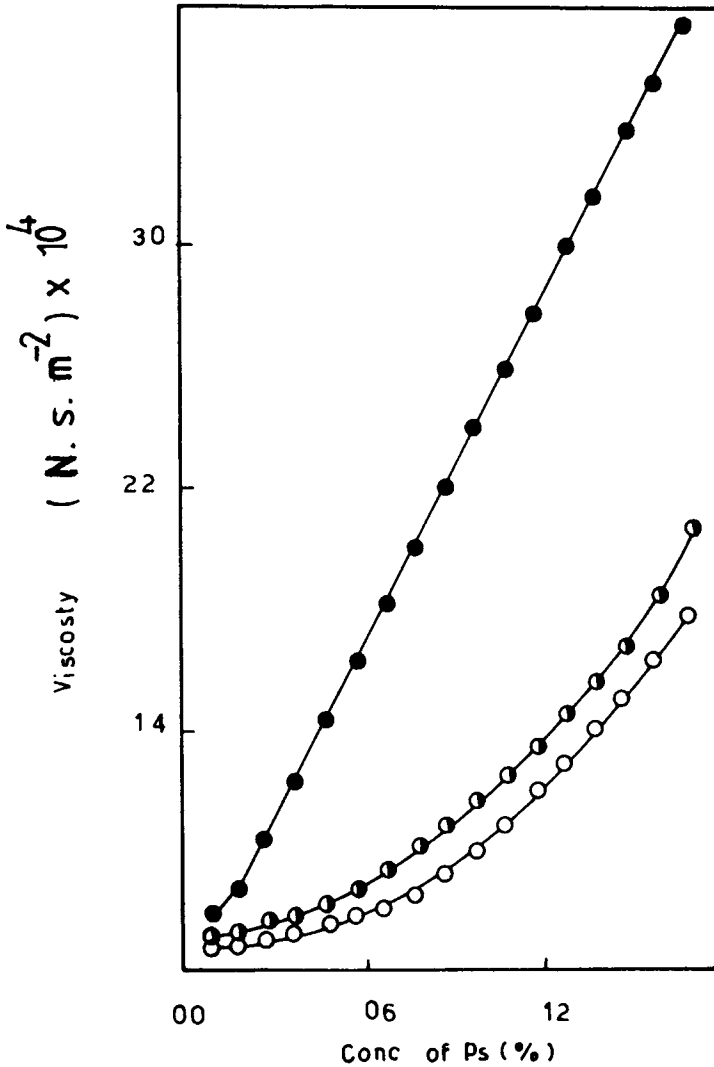


Fig. 3. Linear increase of viscosity with increasing concentration of PS in different solvents: ○ benzene, ◐ toluene, and ● THF.

where C is the measured velocity of sound in the polymer solution and P is its measured density. Attenuation data (α/f^2) were obtained at a frequency (f) of 2 MHz. Shear relaxation was calculated using the following equation:

$$f^2/\alpha = 3PC^3/8\pi\eta_s \quad (2)$$

where η_s is the shear viscosity of polymer solution and β is the ultrasound absorption coefficient. The accuracy of the absorption coefficient was better than $\mp 1.5\%$. Relaxation time (τ) was calculated as follows:

$$\tau = 3PC^2/4\eta_s \quad (3)$$

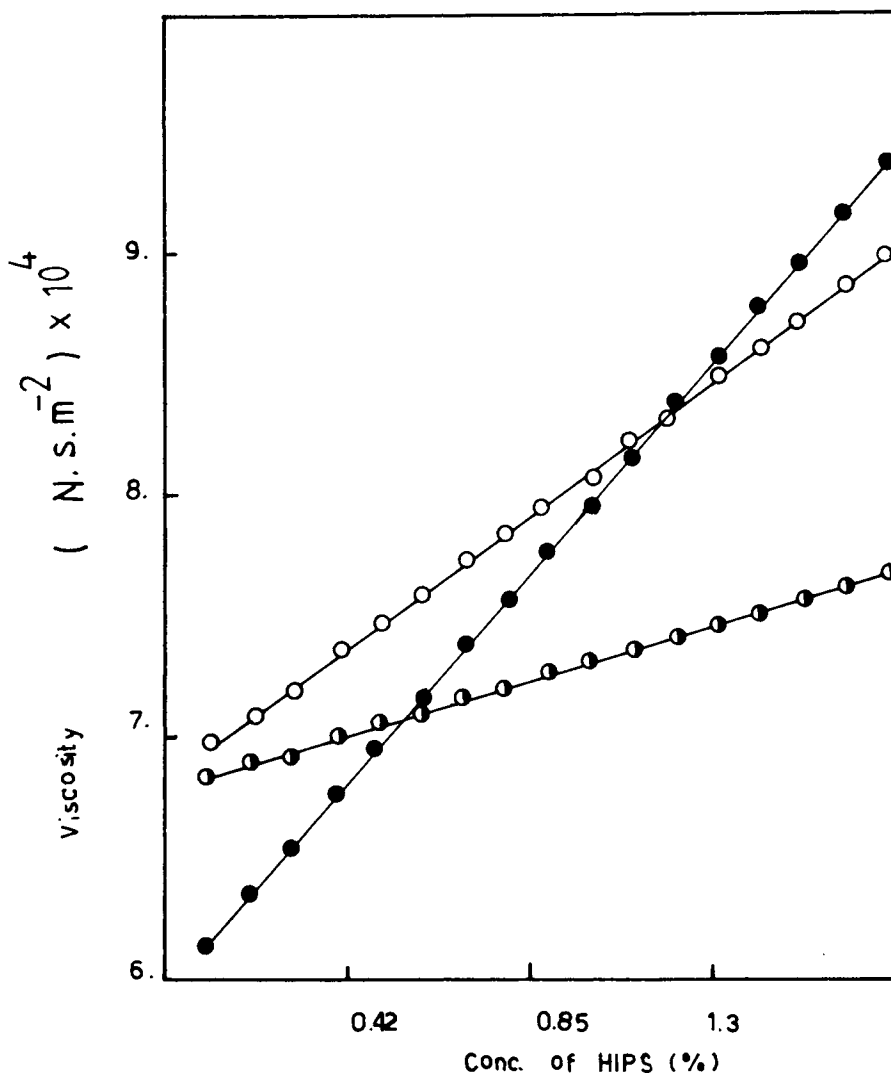


Fig. 4. Linear increase of viscosity with increasing concentration of HIPS in different solvents: ○ benzene, ◐ toluene, and ● THF.

Molecular weight (\bar{M}_n , \bar{M}_w , and \bar{M}_z) and the molecular weight distribution of PS and HIPS (Table I) were determined using a water associate 150°C gel permeation chromatograph (Milford, Massachusetts). Details of the measurements are similar to those described recently.¹⁰

RESULTS AND DISCUSSIONS

The densities of PS and HIPS show normal increase with concentration increase in benzene, toluene, and THF (Figs. 1 and 2); also viscosities increased with concentration increase. This demonstrates the action of the physical entanglement of high molecular weight polymer, unlike the behavior of simple

TABLE II
Effect of Solvents on the Intrinsic Viscosities of PS and HIPS at 298.15 K

Solvent	PS [η]	HIPS [η]
THF	0.60	0.36
Benzene	0.61	0.39
Toluene	0.65	0.44

liquid.¹¹ The density of PS-THF was more than PS-toluene and PS-benzene, respectively, whereas in HIPS the highest density was of the HIPS-benzene and the lowest of toluene. The viscosity of HIPS solution at different concentration shows a rather different behavior. HIPS-tetrahydrofuran starting at

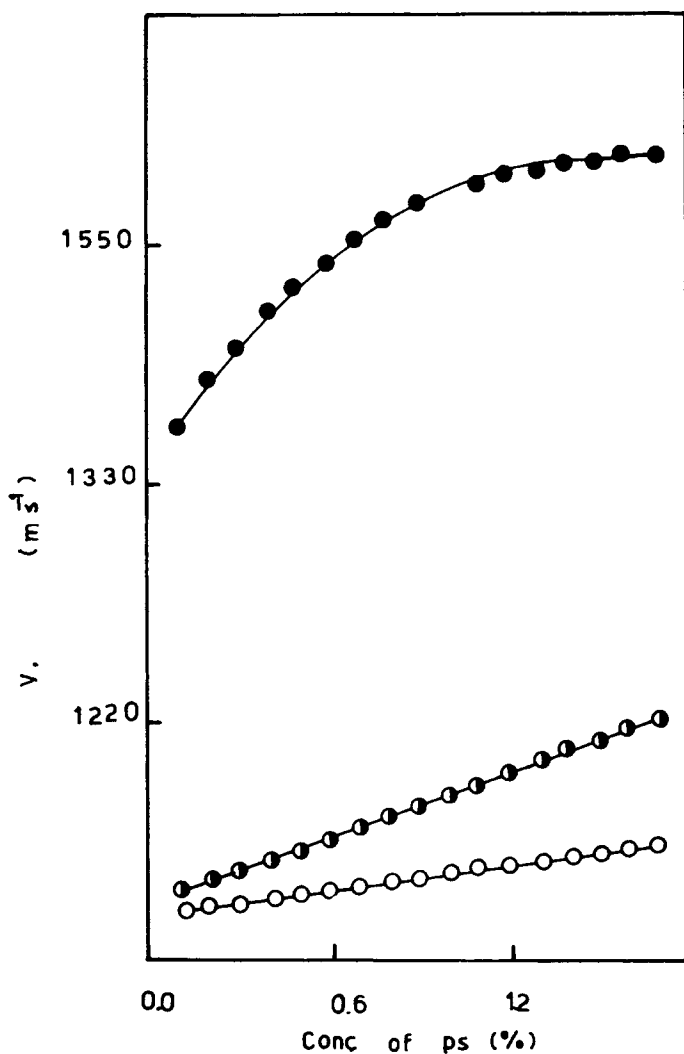


Fig. 5. Linear increase of velocity with increasing concentration of PS in different solvents: \circ benzene, \bullet toluene, and \bullet THF.

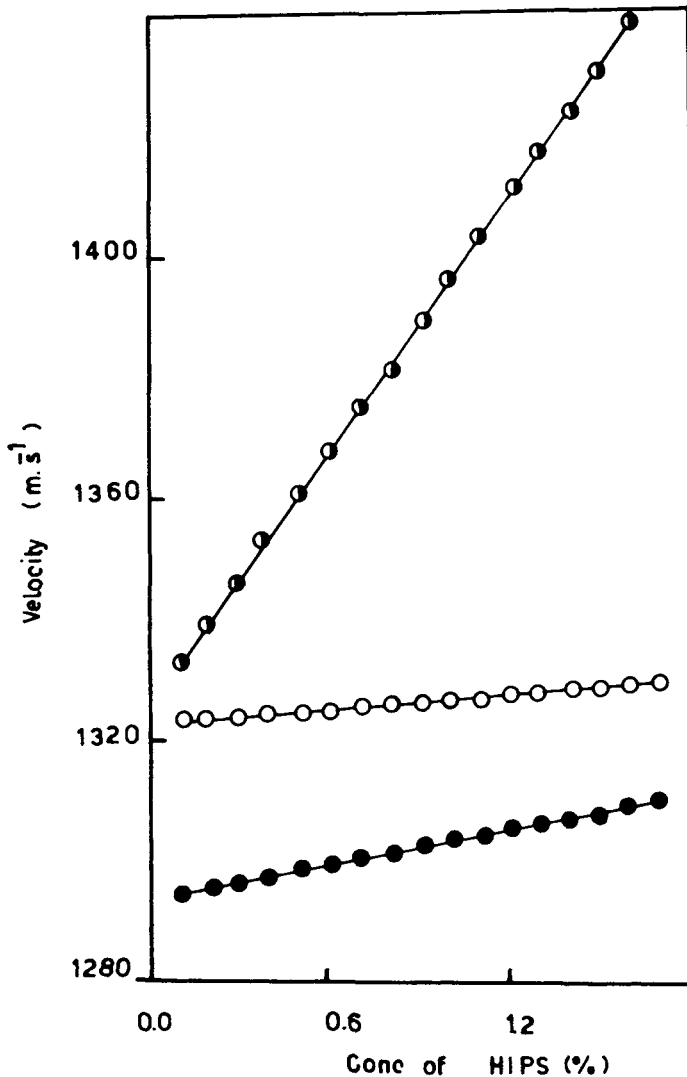


Fig. 6. Linear increase of velocity with increasing concentration of HIPS in different solvents: ○ benzene, ◐ toluene, and ● THF.

low concentration at the lowest viscosity values, however, with the increase of concentration did crossover the HIPS-toluene and HIPS-benzene plot, respectively (Fig. 3 and 4). This behavior comes from the part of the rubbery phase (butadiene) in HIPS, and thus such simple viscosity measurements of its dilute polymer solution can be used to differentiate it from PS. However, experimental $[\eta]$ values shown in Table II indicated similar behavior of PS and HIPS. The highest $[\eta]$ values were obtained in toluene, whereas the lowest $[\eta]$ were in THF solutions. Although these results demonstrate indirectly the solvent effect on the $[\eta]$, it did not show abnormal deviation resulting from the rubbery phase of HIPS. This is because $[\eta]$ is determined at infinite dilution. $[\eta]$ in this work was determined from the plot of η_{sp}/C vs. C where η_{sp} is the specific viscosity of polymer solution of concentration C :

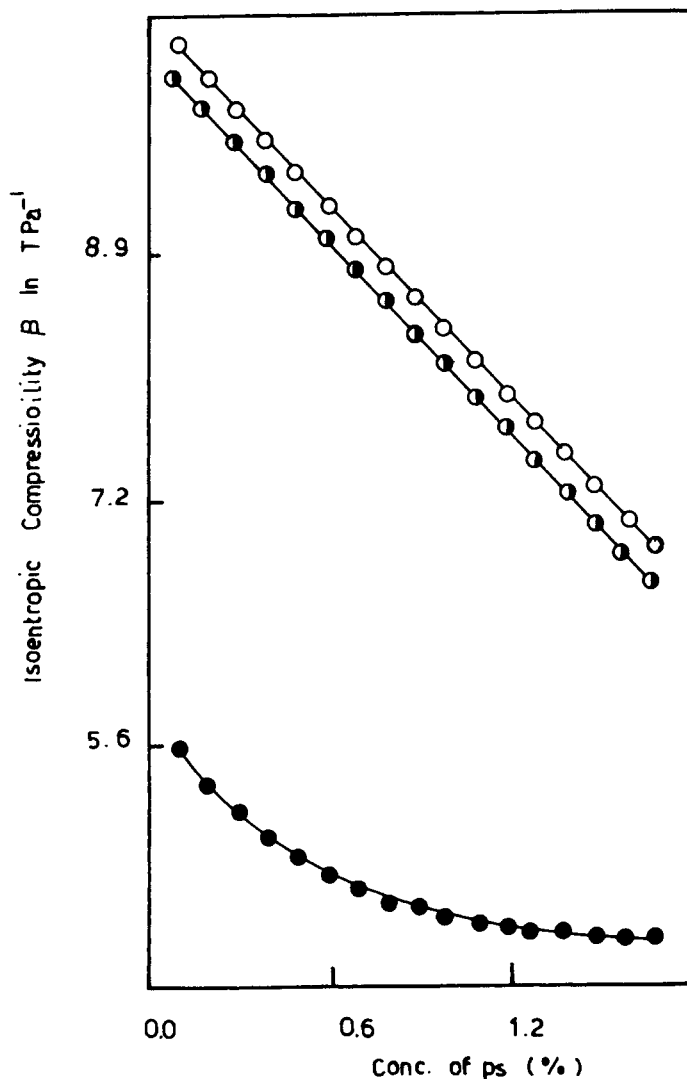


Fig. 7. Linear decrease of isoentropic compressibility with increasing concentration of PS in different solvents: \circ benzene, \bullet toluene, and \bullet THF.

$$\eta_{sp} = \frac{t}{t_0} - 1 \quad (4)$$

where t_0 and t are the efflux times of pure solvent and dilute polymer solution, respectively. The plot of η_{sp}/C vs. C yielding a straight line whose intercept and gradient render the values of $[\eta]$ and k (Huggins constant):

$$C/\eta_{sp} = [\eta] + k[\eta]^2C \quad (5)$$

The increase of the velocity of sound for 15 different concentrations of PS and HIPS in the three different solvents are shown in Figures 5 and 6. The velocity

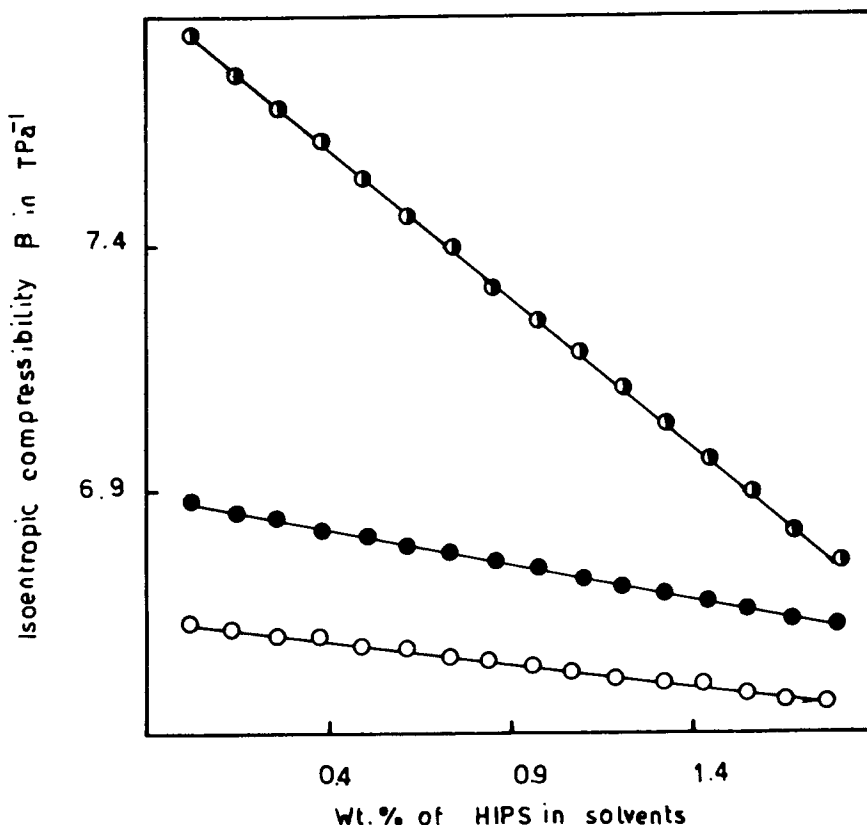


Fig. 8. Linear decrease of isentropic compressibility with increasing concentration of HIPS in different solvents: ○ benzene, ◐ toluene, and ● THF.

of sound propagation was used to calculate the isentropic compressibility (β), and the decrease in β for the different 15 concentrations of solvents are shown in Figures 7 and 8, respectively. Figure 5 shows that the highest values for the velocity of sound were obtained for PS in THF, whereas the highest value of the velocity of sound for HIPS were determined in toluene (Fig. 6). The lowest values of the velocity of sound for PS solutions were obtained in benzene (Fig. 5) and for HIPS solution in THF. Figures 7 and 8 show that in general it appears that the excess negative isentropic compressibility associated with HIPS solutions is less than that with the PS counterparts. This can be interpreted to the rubbery phase of HIPS and moreover to the solvation of the polymer chains. Apparently, the interaction of HIPS chains with solvent is somewhat less than that of PS, also due to butadiene segments. The lower interaction of HIPS macromolecules with solvent could only be due to the inclusion of incompatible butadiene. The nature of solvent interaction with polymer backbone has been the subject of interesting earlier observation.¹²

The increase of polymer concentration was accompanied by an increase in relaxation time for both PS and HIPS as shown in Figures 9 and 10. The interaction causing associations between the polymer molecules and the solvent molecules are responsible for the increase in relaxation time for both PS and HIPS. Such interaction was indeed also the reason for the increase in the

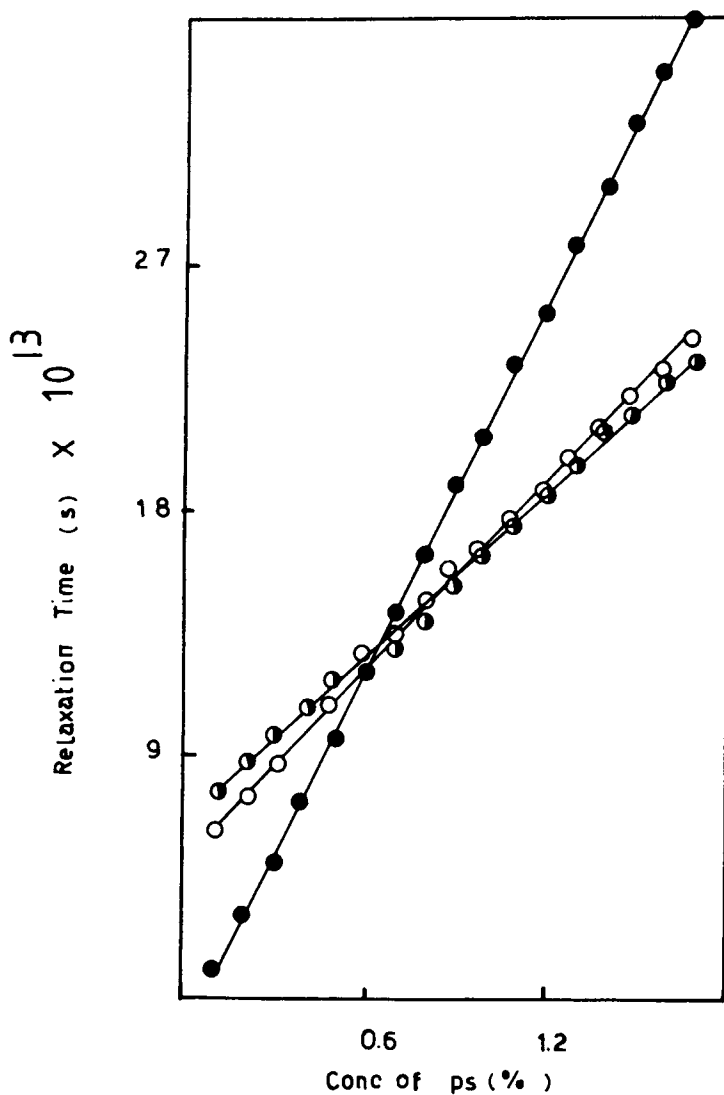


Fig. 9. Linear increase of relaxation time with increasing concentration of PS in different solvents: \circ benzene, \ominus toluene, and \bullet THF.

ultrasonic velocity (Figs. 5 and 6). It is well known that macromolecules may influence each other indirectly by way of mutual interactions.¹ Interaction with solvent molecules is a phenomenon referred to as hydrodynamic screening¹³ and is significant in determining the viscous flow properties of rather dilute polymer solution.

CONCLUSIONS

The applicability of ultrasonic technique to the determination of polymer-solvent interaction has been demonstrated for PS and HIPS. Little change in the structure of the polymer influence the behavior of its polymer solutions.

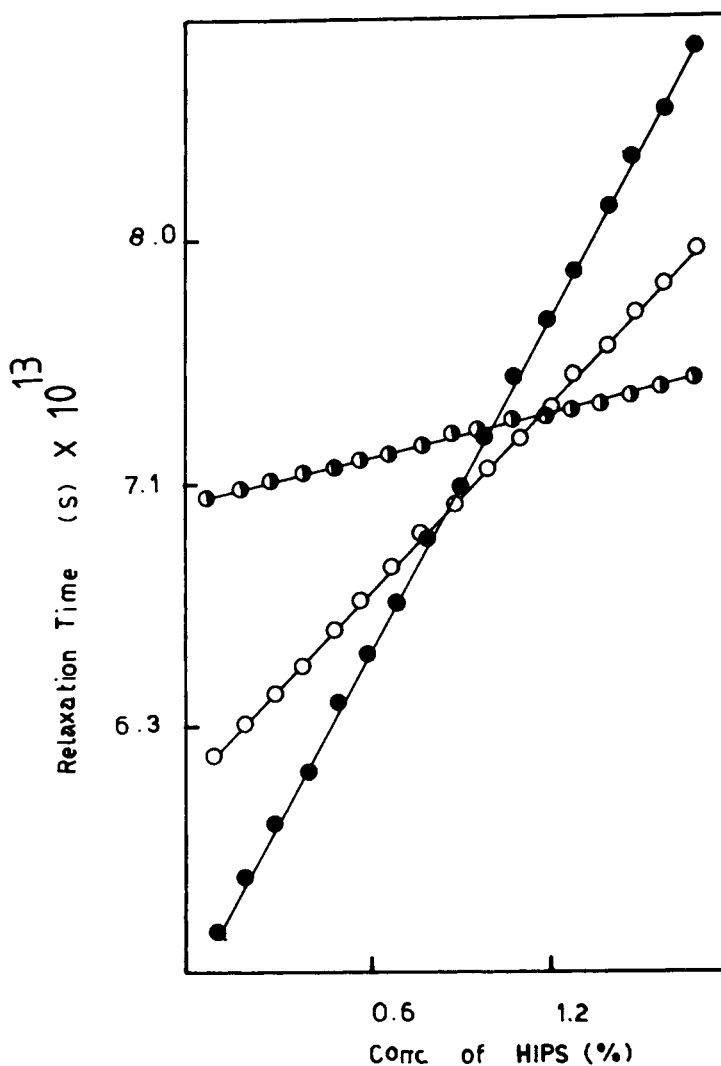


Fig. 10. Linear increase of relaxation time with increasing concentration of HIPS in different solvents: \circ benzene, \bullet toluene, and \bullet THF.

Being fast, nondestructive and versatile, ultrasonic technique is useful for testing structure-property relationships of industrial polymers.

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