

# Miscibility, density and viscosity of polystyrene in *n*-hexane at high pressures

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The demixing pressures, densities and viscosities of solutions of nearly monodisperse polystyrene samples ( $M_w/M_n < 1.1$ ) in *n*-hexane have been determined. Measurements were conducted with samples of different molecular weights ( $M_w = 4000$ – $50\,000$ ) at concentrations up to 8 mass% over a pressure range from 5 to 70 MPa and a temperature range from 323 to 423 K. The demixing pressures were observed to increase with molecular weight (from about 10 MPa for  $M_w = 4000$  to 50 MPa for  $M_w = 50\,000$ ) and show high sensitivity to temperature ( $\Delta P/\Delta T$  being about  $-1 \text{ MPa } ^\circ\text{C}^{-1}$ ) in the range investigated. Density and viscosity data were collected in the one-phase homogeneous regions, and viscosity was correlated with an equation of the form  $\eta = A \exp\{B/(1 - V_0\rho)\}$ , which is based on the free-volume considerations. For a given system, the viscosities increase with solution density (or pressure). At a fixed solution density, viscosity increases with polymer concentration or molecular weight. Depending upon the system, viscosities have ranged from 0.15 to 0.45 mPa.s. Flow activation volumes and flow activation energies were about  $40 \text{ cm}^3 \text{ mol}^{-1}$  and  $6 \text{ kJ mol}^{-1}$ , respectively. The demixing and viscosity data have been also compared with the results obtained in *n*-butane and *n*-pentane for one sample ( $M_w = 9000$ ). In going from *n*-butane to *n*-hexane, the demixing pressures decrease while the viscosities become higher. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Recent advances in the possible use of near-critical and supercritical fluids as process or processing fluids in polymer synthesis and modifications have increased the need for basic and applied data on the thermodynamic and transport properties of polymer solutions at high pressures<sup>1</sup>. For successful design of new processes using supercritical fluids, information on equilibrium properties (such as miscibility and demixing conditions, and phase compositions), and non-equilibrium characteristics (such as the dynamic aspects of dissolution and phase separation) and transport properties (in particular diffusivities and viscosities) are needed.

Viscosity is indeed an important parameter, which influences not only the usual mixing and flow conditions and effectiveness of the heat and/or mass transfer operations, but also the kinetics of phase separation which are important to many applications, such as spray coating, foaming, spinning (i.e. fibre formation), and manufacturing composite materials, membranes and other porous materials<sup>1,2</sup>.

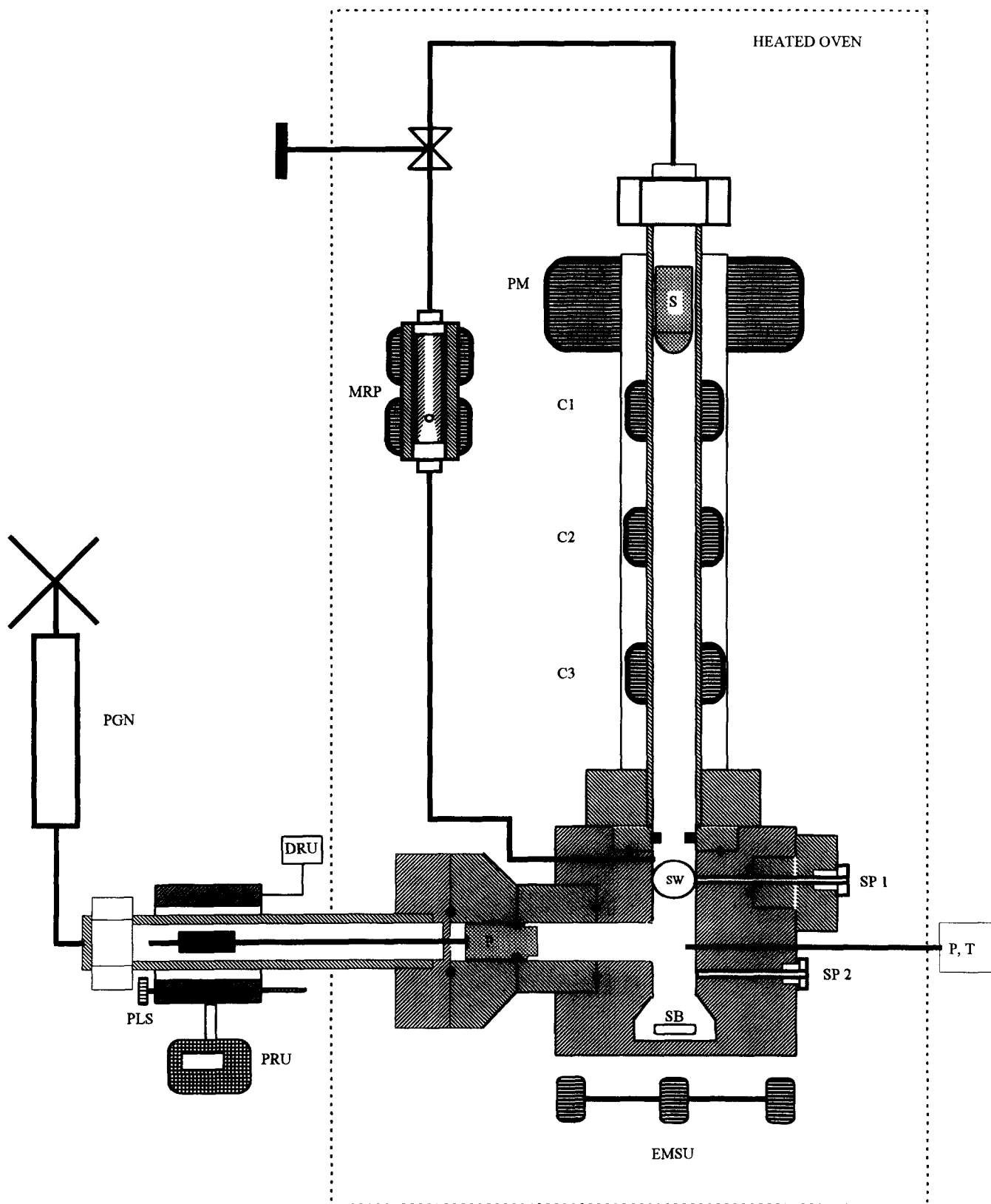
From a fundamental perspective, viscosity measurements are used to gain insight into polymer–solvent interactions. The degree of polymer-chain expansion or coiling (or chain collapse) depends on the quality of the solvent which can be altered by changing the temperature, pressure, or the solvent composition. Determination of the intrinsic viscosity as phase separation conditions are approached is one methodology to determine the changes in the radius of gyration and thus the chain dimensions<sup>3</sup>.

An equally important consideration is the influence of viscosity on non-equilibrium processes, such as those encountered in the transient stages during phase separation from polymer solutions. For example, at high viscosities, the typical hydrodynamic effects<sup>4</sup> encountered in fluid mixtures involving small molecules may be suppressed, and phase separation may be retarded<sup>5</sup>. Also, the viscosity asymmetry of the constituents of the polymer solutions (i.e. long chain polymers and small molecule solvents) influence the resulting morphologies in phase separated systems (i.e. isolated droplets of one phase dispersed in the bulk of the other phase, or interconnected bi-continuous network structures<sup>5,6</sup>). Indeed, for systems undergoing phase separation from high pressure solutions by pressure quench or temperature quench<sup>7</sup>, in addition to quench-depth and the rate of penetration into the two-phase regions, viscosity, along with interfacial tension, is an important parameter influencing the progress of phase separation.

We have recently reviewed the available viscosity data for polymer solutions in near-critical and supercritical fluids<sup>3,8</sup>. Despite the extensive viscosity data at normal pressures, there are essentially no high-pressure viscosity data for polymer solutions prior to 1979. The majority of the data, even though for some systems they cover extreme high pressures (up to 20 000 bar), are at relatively low temperatures. It is only recently that viscosity data for polymer solutions are being reported at high pressures, covering a wider range of temperatures<sup>3,8,9</sup>.

Several studies on the viscosity of polystyrene solutions at high pressures have been reported in the literature. These include viscosity data in *trans*-decahydro naphthalene<sup>10</sup>, in *t*-butyl acetate<sup>11</sup>, and in cyclohexane, cyclopentane,

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**Figure 1** Experimental system for measurement of demixing pressures, densities and viscosities. MRP, magnetic recirculation pump; PM, pull-up magnet; S, sinker; C1–C3, LVDT coils; SW, sapphire window; SB, magnetic stirring bar; EMSU, electromagnetic stirring unit; P,T, pressure and temperature sensor; SP1, solute loading port; SP2, solvent loading port; P, movable piston; DRU, digital readout unit; PLS, position locator; PRU, position readout unit; PGN, pressure generator

diethylmalonate, and 1-phenyldecane<sup>12</sup>, which are reported at pressures up to 100 MPa in the temperature range 275–305 K. These studies, which are at conditions far removed from the critical temperatures of the solvents, were conducted using a rotating cylinder viscometer. In

a further study, the viscosity of polystyrene in *t*-butyl acetate was determined at higher pressures (up to 400 MPa) and temperatures (up to 403 K), using a rolling ball viscometer<sup>13</sup>. A rolling ball viscometer was also used for the measurement of viscosities of polystyrene–*trans*

decalin solutions up to 30 MPa in the temperature range 293–318 K<sup>14</sup>. More recently, the viscosity of polystyrene ( $M_w < 9000$ ) was determined in near-critical and super-critical *n*-butane and *n*-pentane at pressures up to 70 MPa in the temperature range 398–443 K<sup>3,15–17</sup>. The results were correlated by the density of the solutions.

The present paper presents the results of a systematic study of solutions of polystyrene in *n*-hexane. The experimental conditions cover a pressure range from 5 to 70 MPa, and a temperature range from 323 to 443 K.

## EXPERIMENTAL

### Materials

The nearly monodisperse polystyrenes samples ( $M_w = 4000, 8000, 9000, 13000, 25000$  and  $50000$ ) with low polydispersities ( $M_w/M_n \leq 1.06, 1.09, 1.06, 1.06, 1.06$ , respectively) were obtained from Scientific Polymer Inc. (Ontario, New York). The solvent, *n*-hexane (99+ % purity) was obtained from Aldrich and used without further purification.

### High pressure view cell and viscometer

Figure 1 shows the schematic diagram of the unique experimental system used to determine demixing pressures, densities and viscosities, all in the same instrument at pressures up to 70 MPa and at temperatures up to 200°C. Operational and design details of this system have been described in previous publications<sup>9,16,17</sup>. Briefly, it consists of: (1) a view-cell equipped with two sapphire windows (SW) for visual observation of the demixing conditions; (2) a piston attachment with position sensing and read-out unit to determine the internal volume of the cell and hence the density of the solution at any temperature and pressure; (3) a fall-tube and sinker attachment with sensing coils to follow the fall time for the sinker and hence to determine the viscosities; (4) a magnetic coil to bring back and hold the sinker in position prior to fall-time measurements; (5) a magnetic circulation pump. All of these are enclosed in a heated oven.

After loading the polymer and solvent, the system pressure and temperature are adjusted to bring about complete miscibility. Pressure is controlled by the pressure generator (PGN) through the movement of a piston inside the variable-volume part of the view cell. The magnetic recirculation pump (MRP) and the electromagnetic stirring unit (EMSU) facilitate the dissolution process and help maintain homogeneity. The electromagnetic stirring unit is made of four magnetic coils, which are sequentially turned on and off to drive the rotation of the stirring bar (SB). The position of the movable piston (P) and hence the internal volume of the cell is determined by a LVDT and a digital read-out unit (DRU)<sup>16,18,19</sup>.

In determination of the demixing pressures, starting from the homogeneous conditions, the pressure is reduced until the cloud points are reached at each temperature. For viscosity determinations, the system pressure is increased to above the demixing pressure conditions, and then the fall-time of the sinker is determined. When the sinker falls through the tube upon deactivation of the magnetic coil, its movement generates an induced voltage change of the LVDT coils ( $C_1, C_2, C_3$ ) positioned along the fall-tube which is recorded by a computer. The response from these coils has the characteristics shown in Figure 2. The fall-time for the sinker from one coil to the other is determined as

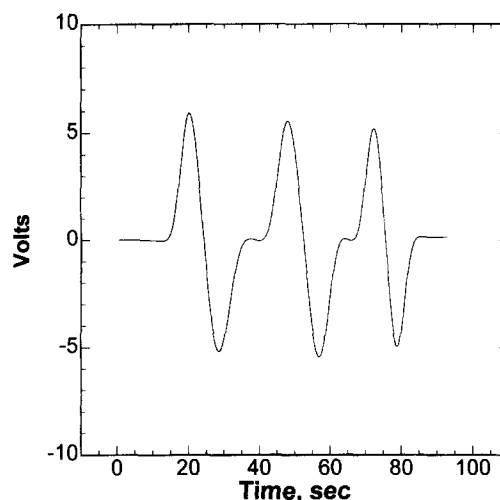


Figure 2 Typical signal output from the three LVDT coils along the fall-tube as the sinker passes through the coils  $C_1, C_2$  and  $C_3$  (see Figure 1)

the time interval between the points where the voltage crosses zero in passing through each coil. The readings from  $C_2$  to  $C_3$  are normally used as the fall-time to determine the viscosity from a calibration relationship  $\eta = K(\rho_s - \rho)t$ , where  $\rho_s$  and  $\rho$  are the densities of the sinker and fluid respectively,  $t$  is the fall-time, and  $K$  is the calibration constant<sup>8</sup>. The accuracy of this system is  $\pm 1\%$  for the density and  $\pm 3\%$  for the viscosity, at pressures up to 70 MPa and at temperatures up to 200°C.

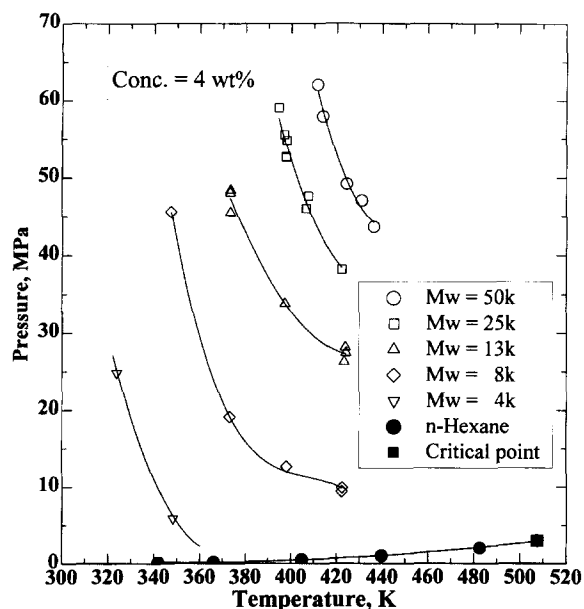
## RESULTS AND DISCUSSION

### Demixing pressures

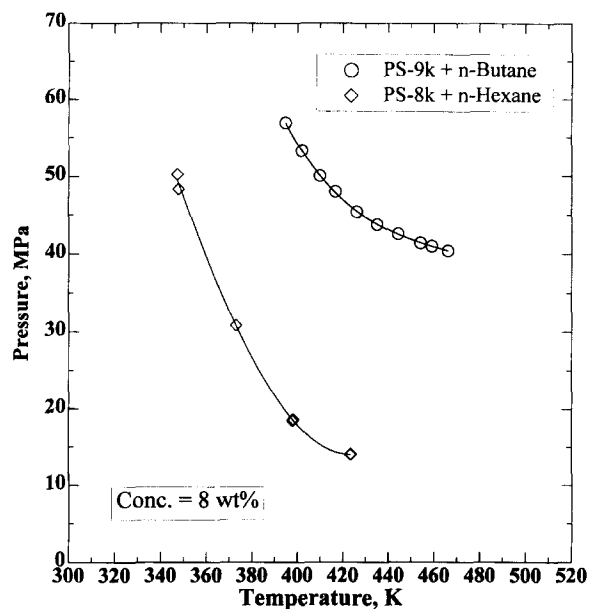
Demixing pressures were determined at a polymer concentration of 4 mass% for the different molecular weight samples. For the polymer with  $M_w = 8000$ , demixing pressures were also determined at several concentrations up to 8%.

Figure 3 shows the demixing ( $P$ - $T$ ) curves for different molecular weight samples at 4%. The vapour pressure curve for *n*-hexane which ends at the critical point of the solvent is also included. Temperatures that have been investigated are below the critical temperature of the solvent, but the pressures are above critical. The region above each demixing curve corresponds to the one-phase homogeneous region where the polymer and the solvent are completely miscible. As shown, with increasing molecular weight of the polymer, the demixing pressures increase significantly. In going from 4000 to the 50 000 molecular weight sample, demixing pressures increase from about 10 MPa to 50 MPa range. Temperature sensitivity is high for all samples, with a  $\Delta P/\Delta T$  of about  $1 \text{ MPa } ^\circ\text{C}^{-1}$ . The demixing pressures show a decrease with increasing temperature, a characteristic of UCST-type behaviour. In these experiments, the demixing pressures were normally reproducible within  $\pm 2\%$ , however, at low temperatures, due to the steep slope of the  $P$ - $T$  curve, demixing pressures were reproducible only within  $\pm 4\%$ .

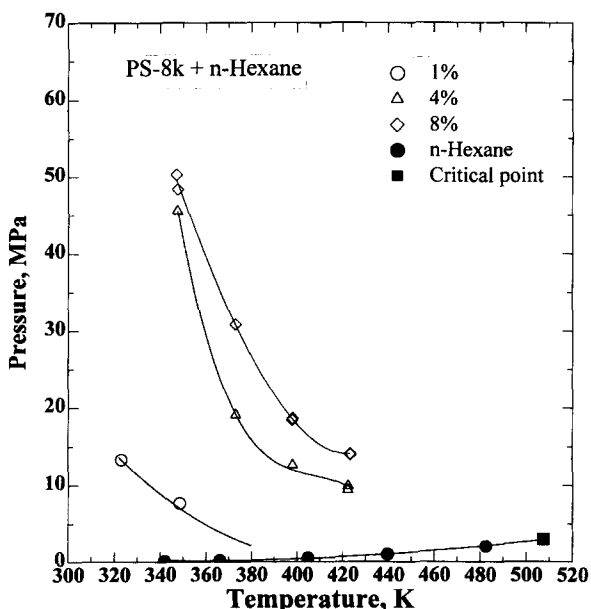
Figure 4 shows the effect of concentration on the demixing pressure for the sample with molecular weight  $M_w = 8000$  in this solvent. As shown, demixing pressures increase with concentration in the range (up to 8%) investigated.



**Figure 3** Demixing pressures for polystyrene solutions (4 mass%) in *n*-hexane as a function of the molecular weight of the polymer. The filled data points represent the vapour pressure for *n*-hexane which terminates at the critical point of *n*-hexane

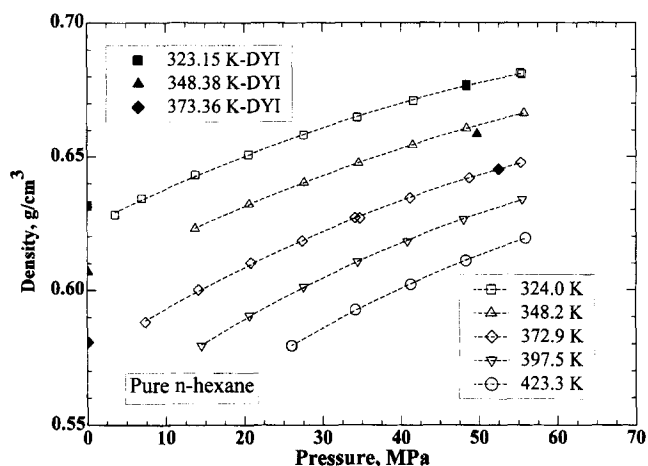


**Figure 5** Comparison of demixing pressures in *n*-butane and *n*-hexane at 8% polymer concentration for polystyrene of similar molecular weights ( $M_w = 8000$  and  $9000$ ). *n*-butane data from ref. 20



**Figure 4** Demixing pressures for polystyrene ( $M_w = 8000$ ;  $M_w/M_n < 1.09$ ) in *n*-hexane as a function of polymer concentration. Concentrations are in mass%

Figure 5 compares the demixing pressures for 8% polystyrene solutions in *n*-butane and *n*-hexane, to show the influence of the alkane chain length. In going from *n*-butane to *n*-hexane, the demixing pressures decrease significantly as a result of the increased dissolving power of the solvent. With higher alkanes, further lowering of the demixing pressures can be expected. Even though the figure shows that the *P*-*T* curves have negative slopes indicative of UCST behaviour, polystyrene + *n*-butane and polystyrene + *n*-pentane mixtures are known to display LCST behaviour in the high temperature regions depending upon the molecular weight and/or the polymer concentration<sup>1,20</sup>. In the temperature range investigated in the present study, polystyrene + *n*-hexane solutions show



**Figure 6** Density of *n*-hexane as a function of pressure at different temperatures. Filled symbols (DYI) are literature data from ref. 21

UCST behaviour, but it is very likely that at higher temperatures, LCST-type behaviour can be observed with this system also.

*Density and viscosity*

Results of density measurements for pure *n*-hexane are shown in Figure 6 at five temperatures in the range from 324 to 423 K and at pressures up to 55 MPa. Literature data<sup>21</sup> at similar temperatures are also included for comparisons. Despite the small differences in temperatures, the agreement is within 1% which is in the accuracy range achievable with the present instrument.

Figures 7-9 show the density data at 4% polymer concentration for samples with molecular weights  $M_w = 8000$ ,  $13000$  and  $25000$ . Figures 10 and 11 show the data at 1 and 8% concentrations for solutions of the sample with molecular weight  $M_w = 8000$ . All density measurements were conducted in the one-phase homogeneous regions of the solutions.

Viscosity measurements were conducted in the temperature range from 323 to 423 K, at 15 K intervals. Figure

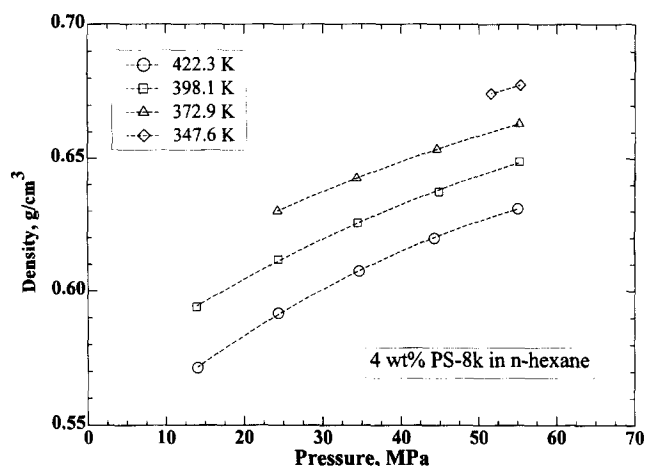


Figure 7 Variation of the density of polystyrene ( $M_w = 8000$ ) solutions (4%) in *n*-hexane with pressure at selected temperatures

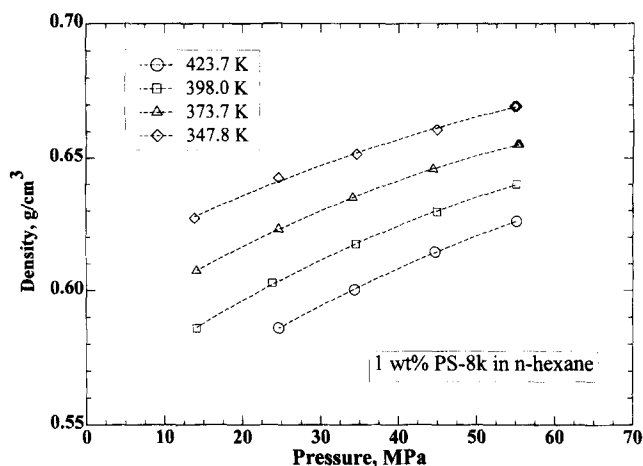


Figure 10 Variation of the density of polystyrene ( $M_w = 8000$ ) solutions (1%) in *n*-hexane with pressure at selected temperatures

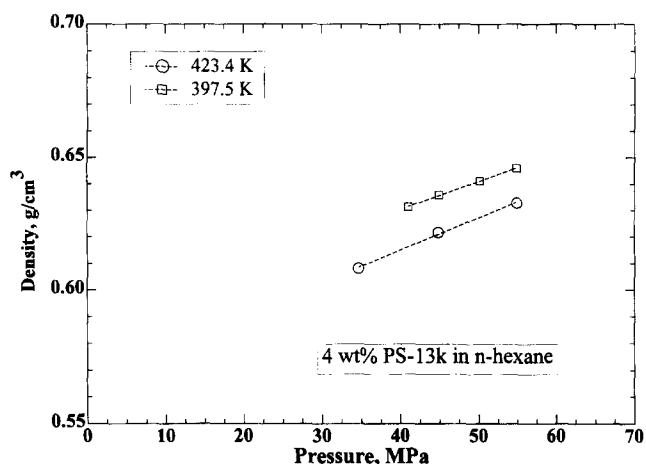


Figure 8 Variation of the density of polystyrene ( $M_w = 13000$ ) solutions (4%) in *n*-hexane with pressure at selected temperatures

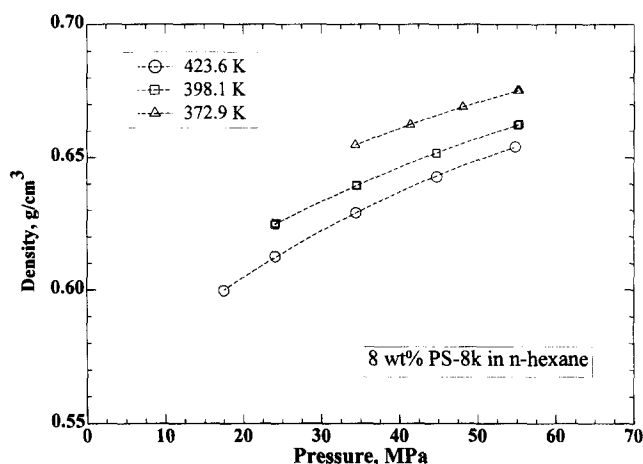


Figure 11 Variation of the density of polystyrene ( $M_w = 8000$ ) solutions (8%) in *n*-hexane with pressure at selected temperatures

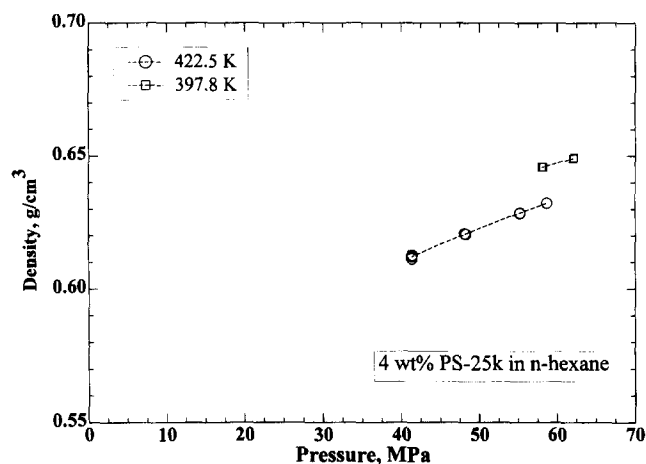


Figure 9 Variation of the density of polystyrene ( $M_w = 25000$ ) solutions (1%) in *n*-hexane with pressure at selected temperatures

12 shows the results for *n*-hexane, along with data from the literature<sup>21,22</sup> for comparisons. Overall, the agreement is within about 3%.

Figures 13–15 show the results for polymer solutions (molecular weights  $M_w = 8000$ , 13 000 and 25 000) at a fixed concentration (4% by mass). Figures 16 and 17 show the results for the solutions ( $M_w = 8000$ ) at two

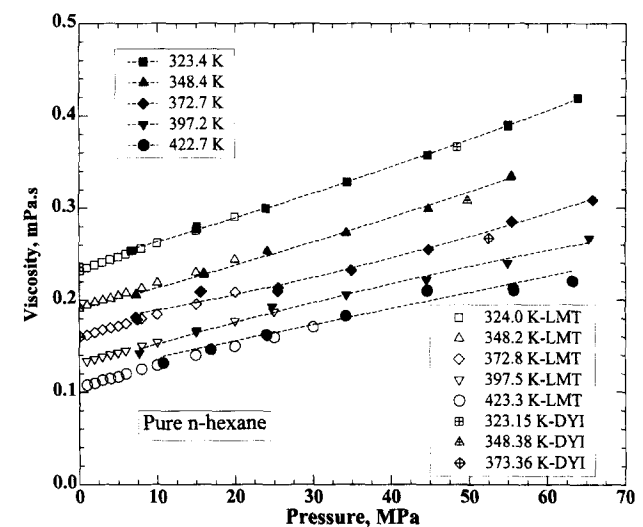


Figure 12 Variation of the viscosity of *n*-hexane with pressure at selected temperatures. Open symbols are literature data from refs 21 (DYI) and 22 (LMT)

additional concentrations. The figures display the expected trends. The viscosity increases with increasing pressure and the polymer concentration, but decreases with increasing temperature.

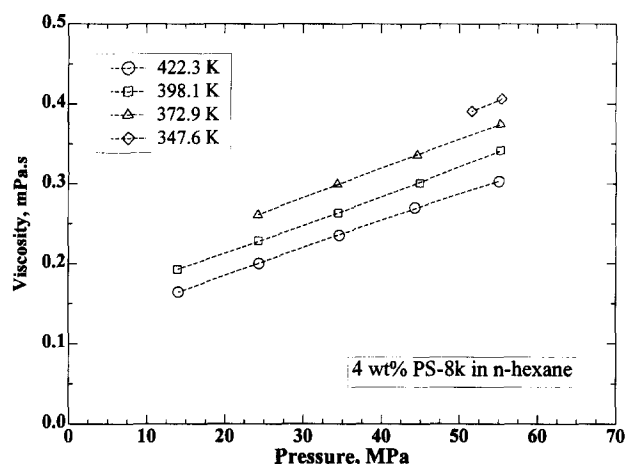


Figure 13 Variation of the viscosity of polystyrene ( $M_w = 8000$ ) solutions (4%) in *n*-hexane with pressure at selected temperatures

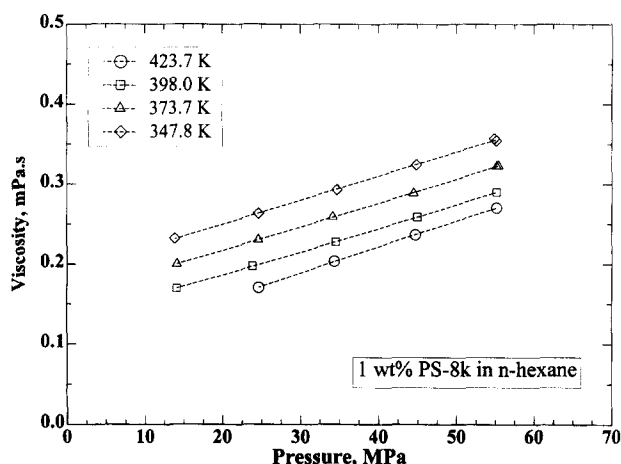


Figure 16 Variation of the viscosity of polystyrene ( $M_w = 8000$ ) solutions (1%) in *n*-hexane with pressure at selected temperatures

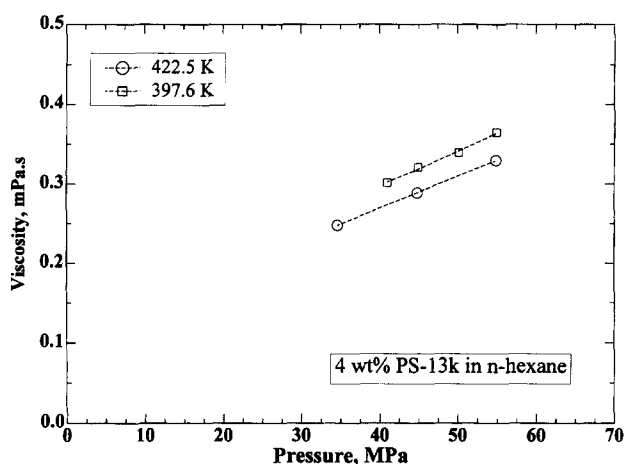


Figure 14 Variation of the viscosity of polystyrene ( $M_w = 13000$ ) solutions (4%) in *n*-hexane with pressure at selected temperatures

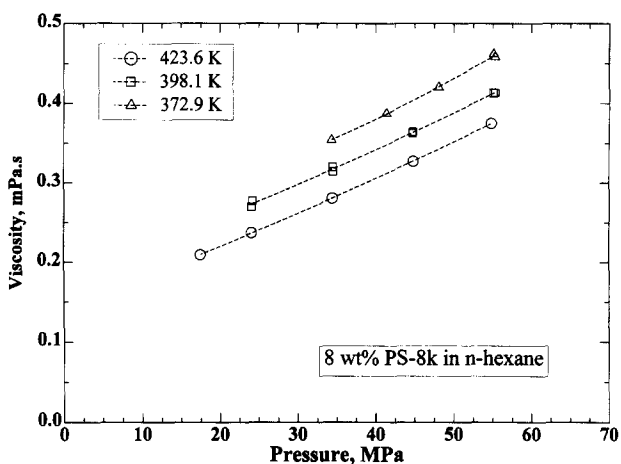


Figure 17 Variation of the viscosity of polystyrene ( $M_w = 8000$ ) solutions (8%) in *n*-hexane with pressure at selected temperatures

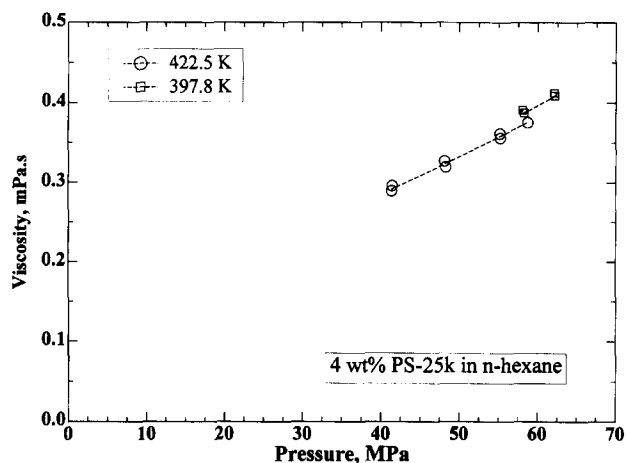


Figure 15 Variation of the viscosity of polystyrene ( $M_w = 25000$ ) solutions (4%) in *n*-hexane with pressure at selected temperatures

*Variation of viscosity with pressure.* Variation of viscosity with pressure can be described according to the following relationship:

$$\eta = A \exp\{V^\# P/RT\} \quad (1)$$

where  $\eta$  is the viscosity,  $V^\#$  the flow activation volume,  $R$  the gas constant,  $P$  the pressure,  $T$  the temperature and

$A$  is a prefactor<sup>8,9</sup>. The present data for *n*-hexane and solutions of polystyrene have been correlated using equation (1), and the flow activation volumes have been determined from slopes of the plots of  $\ln \eta$  vs  $P$ . They are summarized in Table 1. Since the accessible pressure range for complete miscibility varies for each polymer solution, the flow activation volumes have been evaluated using viscosity data in the pressure range indicated for each molecular weight sample.

The flow activation volumes that are calculated range from 34 to 49  $\text{cm}^3 \text{mol}^{-1}$ . Even though the values appear to show some increase with increasing molecular weight or concentration of the polymer, or with a decrease in temperature, it is difficult to generalize. Evaluation of the flow activation volumes for other alkanes and for solutions of polystyrene in *n*-butane and *n*-pentane indicates that the activation volumes are of the same order of magnitude<sup>23</sup>. For example, at 423 K,  $V^\#$  varies from 36.3 to 34.4  $\text{cm}^3 \text{mol}^{-1}$ , and at 398 K, the variation is from 32.5 to 37.2  $\text{cm}^3 \text{mol}^{-1}$  in going from butane to hexane. For 1% solutions of PS ( $M_w = 9000$ ), the values range from 30.3 to 36.3  $\text{cm}^3 \text{mol}^{-1}$  at 423 K and from 35.4 to 37.8  $\text{cm}^3 \text{mol}^{-1}$  at 398 K in the respective solvents.

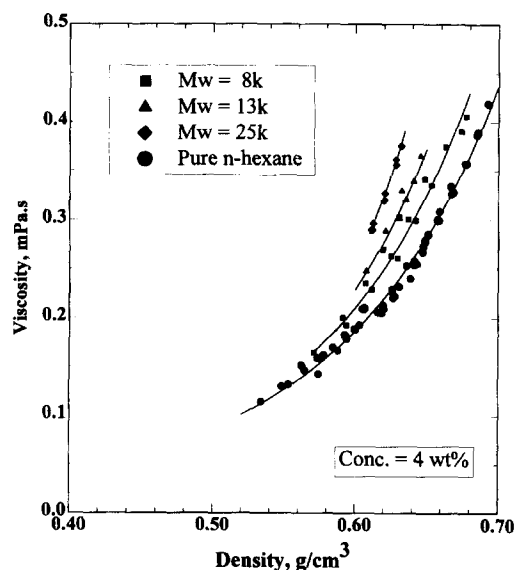
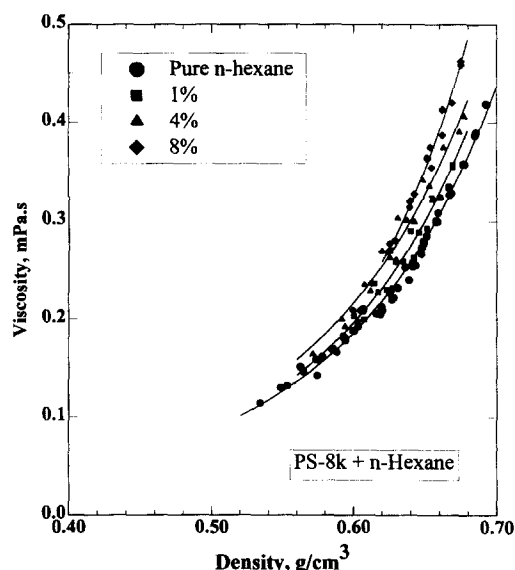
*Variation of the viscosity with temperature.* The temperature dependence of viscosity can be described by the

**Table 1** Activation volume  $V^\ddagger$  ( $\text{cm}^3 \text{mol}^{-1}$ ) for pure *n*-hexane and polystyrene solutions in *n*-hexane

$T$ (K)	<i>n</i> -Hexane (10–55 MPa)	1% PS8k (10–55 MPa)	4% PS8k (15–55 MPa)	8% PS8k (5–55 MPa)	4% PS13k (35–55 MPa)	4% PS25k (45–55 MPa)
423	34.4	36.2	36.3	44.1	46.9	47.1
398	37.2	37.8	38.5	44.2	46.6	48.7
373	39.7	40.5	42.7	48.3		
348	39.4	43.5	43.1			
323	43.5					

**Table 2** Activation energy  $E$  ( $\text{kJ mol}^{-1}$ ) for pure *n*-hexane and polystyrene solutions in *n*-hexane

$P$ (MPa)	<i>n</i> -Hexane (323–423 K)	1% PS8k (348–423 K)	4% PS8k (348–423 K)	8% PS8k (373–423 K)	4% PS13k (398–423 K)
55	4.4	4.6	5.6	5.5	5.5
45	4.8	5.2	5.7		
34	5.4	6.0		6.1	6.1
24	6.1	7.1			
10	7.5				

**Figure 18** Variation of viscosity of polystyrene solutions (4%) in *n*-hexane with the solution density for different molecular weights ( $M_w = 8000, 13000, \text{ and } 25000$ ). Solid curves are the correlations based on free-volume considerations given by equation (3)**Figure 19** Variation of viscosity of polystyrene ( $M_w = 8000$ ) solutions in *n*-hexane with the density of the solution for different concentrations ( $c = 0, 1, 4 \text{ and } 8\%$  by mass). Solid curves are the correlations based on free-volume considerations given by equation (3)

Arrhenius-type relationships, i.e.

$$\eta = A \exp\{E/RT\} \quad (2)$$

where  $E$  is the flow activation energy and  $T$  is the temperature, and  $R$  is the gas constant. From the data shown in Figures 12 to 17, the flow activation energies were calculated from plots of  $\ln \eta$  versus  $1/T$ . The results are shown in Table 2. Just like the case for the calculation of the flow activation volume, the temperature range for the complete miscibility varies with individual polymer solutions, and therefore the flow activation energies listed in the table have been evaluated in temperature range indicated for each solution. The flow activation energies were mostly in the 5–7  $\text{kJ mol}^{-1}$  range. The flow activation energies for polystyrene solutions in *n*-butane and *n*-pentane were previously reported to be about 8  $\text{kJ mol}^{-1}$ .<sup>17</sup>

*Variation of viscosity with density.* Density has been used quite successfully to scale and correlate the viscosity data<sup>3,8,9,15,16</sup>. A number of polymer systems have been correlated using the Doolittle relationship, i.e.

$$\eta = A \exp\{B/(1 - V_0\rho)\} \quad (3)$$

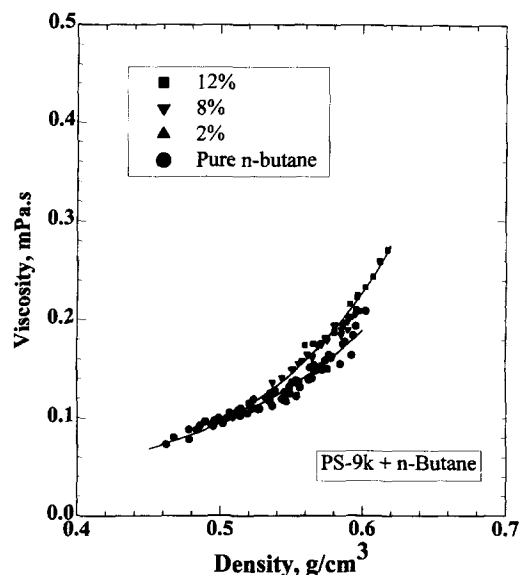
where  $\rho$  is the density,  $A$  and  $B$  are constants, and  $V_0$  is the close-packed volume. Using the density data (Figures 6 to 11), the viscosities of the solutions at different temperatures and pressures were plotted as functions of density, and were correlated using equation (3). The optimal values of the parameters  $A$ ,  $B$ , and  $V_0$  were determined by minimizing the objective function  $F_{\text{obj}} = \sum [\eta_{i,\text{correlation}} - \eta_{i,\text{experimental}}]^2$  in accordance with the Powell's multidimensional direction set method<sup>24</sup>.

Variation of viscosity with density is shown in Figures

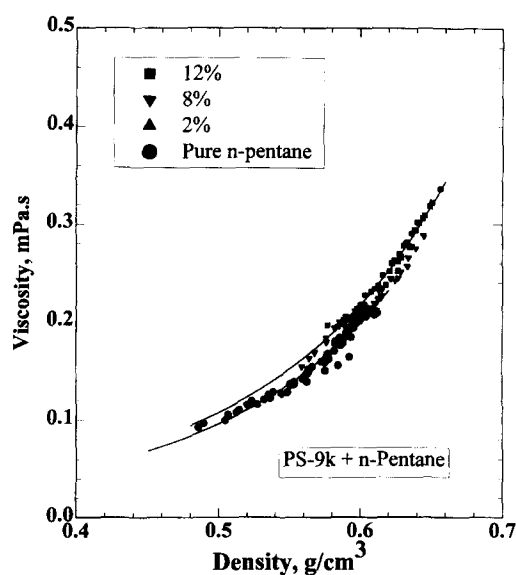
**Table 3** Coefficients of the equation  $\eta = A \exp[B/(1 - V_0\rho)]$  for the density dependence of viscosity of polystyrene solutions in *n*-hexane

$M_w$	Polymer concentration (mass%)	$A$	$B$	$V_0$	SE <sup>a</sup>
	0 ( <i>n</i> -Hexane)	$2.706 \times 10^{-7}$	9.899	0.4393	0.007
8k	1	$2.509 \times 10^{-7}$	9.957	0.4439	0.011
	4	$3.171 \times 10^{-7}$	9.913	0.4370	0.013
	8	$1.619 \times 10^{-7}$	9.960	0.4884	0.008
13k	4	$1.997 \times 10^{-7}$	9.945	0.4795	0.009
25k	4	$6.155 \times 10^{-7}$	10.300	0.5390	0.003

<sup>a</sup> Standard error of estimating the viscosities using the given coefficients,  $SE = \{\sum [y_i - y_{cal,i}]^2/n\}^{1/2}$ , where  $y_i$  and  $y_{cal,i}$  are the experimental and the calculated values, and  $n$  is the number of data points



**Figure 20** Variation of viscosity of polystyrene ( $M_w = 9000$ ) solutions in *n*-butane with the density of the solution for different concentrations ( $c = 0, 2, 8, 12\%$  by mass). Solid curves are the correlations based on free-volume considerations given by equation (3). Data from ref. 16



**Figure 21** Variation of viscosity of polystyrene ( $M_w = 9000$ ) solutions in *n*-pentane with the density of the solution for different concentrations ( $c = 0, 2, 8, 12\%$  by mass). Solid curves are the correlations based on free-volume considerations given by equation (3). Data from ref. 16

**Table 4** Coefficients of the equation  $\eta = A \exp[B/(1 - V_0\rho)]$  for the density dependence of viscosity of polystyrene ( $M_w = 9000$ ) solutions (12% by mass) in *n*-pentane and *n*-butane

	$A$	$B$	$V_0$	SE <sup>a</sup>
<i>n</i> -Butane	$3.494 \times 10^{-7}$	9.908	0.4158	0.007
<i>n</i> -Pentane	$2.985 \times 10^{-7}$	9.980	0.4260	0.007
PS 9k + <i>n</i> -pentane	$3.728 \times 10^{-7}$	9.944	0.4182	0.005
PS 9k + <i>n</i> -butane	$1.975 \times 10^{-7}$	9.963	0.4770	0.006

<sup>a</sup> See Table 3 for explanation

18 and 19. In *Figure 18* the results are presented at 4% concentration for different molecular weights. *Figure 19* shows the results for different concentrations for the sample with molecular weight 8000. The solid curves in the figures are the correlations with parameters as given in *Table 3*. The apparent close-packed volume for *n*-hexane is estimated from these correlations to be about  $0.439 \text{ cm}^3 \text{ g}^{-1}$ . A value of  $0.296 \text{ cm}^3 \text{ g}^{-1}$  was obtained for carbon dioxide, by a similar analysis of viscosity data for carbon dioxide<sup>9</sup>.

We have conducted analyses of the viscosity data for solutions of polystyrene in *n*-butane and *n*-pentane reported earlier<sup>16,17</sup>, according to equation (3) also. The results are shown for the sample  $M_w = 9000$  in *Figures 20* and *21*. The results show that density is indeed an effective scaling parameter for these systems. The correlation

curves are shown for the pure solvents and the 12% polymer solutions which provide a bound for the range of viscosities. For these low molecular weight polymer samples at these concentrations, viscosities are affected only slightly, the dominating factor being the solvent. The parameters are shown in *Table 4*. The apparent close-packed volume is found to be slightly smaller than, but of the same magnitude as, hexane (i.e.  $0.426 \text{ cm}^3 \text{ g}^{-1}$  for pentane,  $0.416 \text{ cm}^3 \text{ g}^{-1}$  for butane).

## CONCLUSIONS

It is shown that demixing pressures can be lowered by going from *n*-butane to *n*-hexane, and that higher molecular weight polystyrene samples can be completely dissolved. In the molecular weight and concentration



range investigated, solutions in *n*-hexane all show upper critical solution type behaviour where demixing pressures decrease with increasing temperature. It is shown that viscosities can be correlated with the density of the solutions. The trends with molecular weight and polymer concentration were as expected, each leading to an increase in the viscosity of the solutions. Activation volumes and activation energies were about  $40 \text{ cm}^3 \text{ mol}^{-1}$  and  $6 \text{ kJ mol}^{-1}$ , respectively.

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