

# High-Pressure Viscosity of Polystyrene Solutions in Toluene + Carbon Dioxide Binary Mixtures

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Received 11 January 1999; accepted 13 June 1999

**ABSTRACT:** High-pressure viscosity of polystyrene ( $M_w = 50,000$ ,  $M_w/M_n \leq 1.06$ ) solutions in toluene and in mixtures of toluene + carbon dioxide was measured using a falling cylinder-type viscometer at 320, 340, and 360 K, and up to 35 MPa. Solutions with polystyrene concentrations of 3, 5, and 7 wt % were investigated. Carbon dioxide levels in the range from 0 to 14.7 wt % were evaluated. Viscosity was observed to vary linearly with pressure at the temperatures and polymer concentrations investigated. Viscosity of the polymer solutions decreased as the concentration of carbon dioxide in the mixture was increased. The largest viscosity reduction was observed at the lowest temperature and at the highest concentration of polymer. The viscosity of the solutions was correlated with the solution density for different compositions. It was found that solutions of the same density have different viscosities, depending upon the carbon dioxide concentration in the mixture. The solutions with the higher carbon dioxide content display the lower viscosities at a given density. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 306–315, 2000

**Key words:** viscosity; high pressure; polystyrene; toluene; carbon dioxide

## INTRODUCTION

The utilization of high-pressure gases or supercritical fluids in processing of polymers has greatly expanded in the past decade. These fluids are used either as solvents or as antisolvents for polymers. When used as solvents, the pressure- and temperature-tunable solvent power of these fluids provides a reliable methodology in polymer purification, fractionation, and processing.<sup>1</sup> As antisolvents, high-pressure gases are used in diverse applications that rely on the alteration of phase boundary of polymer–organic solvent mixtures<sup>2</sup> as in solvent-induced particle formation processes.<sup>3</sup> Studies have also been reported on the phase boundary shift in polymer–organic sol-

vent mixtures in the presence of high-pressure gases that lead to the expansion of the liquid–liquid region that facilitates polymer fractionation.<sup>4</sup> Recent attention has been focused on the morphological modification, as well as crystallization of polymeric materials by using high-pressure gases as antisolvents.<sup>5</sup> These systems are composed of ternary mixtures that are made up of organic solvent, polymers, and a high-pressure gas such as carbon dioxide (CO<sub>2</sub>).

The binary mixtures that consist of an ordinary liquid solvent (good solvent) and high-pressure gas (antisolvent) can be employed to dissolve a polymer with the flexibility of altering the solvent strength towards the polymer. In addition to temperature and pressure, manipulation of the concentration of the antisolvent in the mixture provides an effective method to control the mixing and demixing processes in the polymer solution. The variation of the solvent strength, and hence, the change in polymer–solvent interactions, also affect the

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*Journal of Applied Polymer Science*, Vol. 75, 306–315 (2000)

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CCC 0021-8995/00/020306-10

conformational state of polymer chains that are reflected in the viscosity of the solutions.

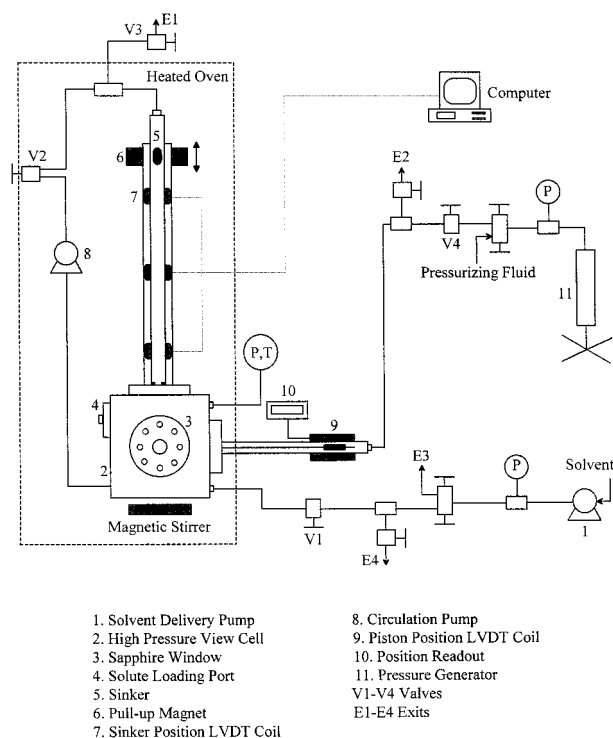
A number of studies on the viscosity of binary mixtures that contain  $\text{CO}_2$  have been reported in the literature. The objectives for these measurements have been varied. For example, the viscosity of supercritical  $\text{CO}_2$  and cosolvent mixtures was determined to provide the necessary information, such as the dimensionless groups for the design of supercritical fluid process equipment.<sup>6</sup> The effect of additives on carbon dioxide viscosity was investigated to evaluate the extent of viscosity increase for enhanced oil recovery.<sup>7</sup> The viscosity of polymer solutions in supercritical  $\text{CO}_2$  has been measured to examine the effect of high pressure on viscosity.<sup>8,9</sup> Most of these systems mainly consist of a high concentration of  $\text{CO}_2$  and relatively low concentrations of the organic solvents or polymeric constituents. More recently, high-pressure  $\text{CO}_2$  is being used to also lower the viscosity of polymer melts.<sup>10,11</sup>

To our knowledge, no data have been previously reported on the viscometric properties of polymer solutions in binary mixtures of an organic liquid solvent and a gas under high pressure. In this study, therefore, the viscosity data of dilute polystyrene solutions in the mixtures of a good solvent (toluene) and an antisolvent ( $\text{CO}_2$ ) have been measured. (Even though at high polymer concentrations carbon dioxide can dissolve in polystyrene and lower its glass transition temperature, carbon dioxide alone is not capable of dissolving polystyrene at modest pressures, and thus is viewed as an antisolvent). The pressure and temperature dependence of the viscosity of polystyrene solutions in pure toluene are also reported. The solution densities and viscosities were determined using a falling cylinder-type viscometer as a function of pressure, temperature, and the concentration of  $\text{CO}_2$  in the solution. The experimental conditions in this study were selected to correspond to the one-phase homogeneous region of this ternary system as reported in the literature.<sup>12</sup> This study broadens the data base for application that involve pressure- and solvent-induced phase separation processes such as those encountered in particle formation processes.

## EXPERIMENTAL

### Materials

The polystyrene sample of weight average molecular weight of  $M_w = 50,000$ , with a polydispersity



**Figure 1** Experimental apparatus for density and viscosity measurements.

of  $M_w/M_n \leq 1.06$  was purchased from the Pressure Chemical Co. Toluene, with a purity of 99.8%, was obtained from the Aldrich Chemical Co. Carbon dioxide, with a minimum purity of 99.8%, was obtained from the Airco Co. All the materials were used without further purification.

### High-Pressure Viscometer

Figure 1 shows the schematic diagram of the falling cylinder-type high-pressure viscometer. This home-made viscometer permits the simultaneous measurement of density and viscosity of polymer solutions up to 470 K and 70 MPa.<sup>9,13</sup> The apparatus is equipped with two view windows (3) that permit the observation of the phase state of the cell content. For density measurements, the position of a movable piston is determined by using a LVDT (linear variable differential transformer) coil (9). The movement of the sinker in the fall-tube is followed by the three LVDT coils (7) to measure the fall time, and hence, to determine the viscosity of the solution. A pull-up magnet (6) is used to bring the sinker to the top position of the fall-tube. A high-pressure circulation pump (8) is used to circulate the internal solution to maintain the temperature and concentration ho-

mogeneous. Details of the design and operating procedure can be found in our previous articles.<sup>9,13</sup>

### Viscosity Measurements

Density and viscosity measurements were carried out with the solutions of polystyrene ( $M_w = 50,000$ ) in pure toluene as well as in toluene + CO<sub>2</sub> mixtures. First, a measured amount of the polystyrene sample is charged to the cell through the solute loading port (4). The system is then purged several times with gaseous CO<sub>2</sub> to remove air that may have been trapped inside the cell. A known amount of toluene is charged to achieve a desired concentration of the cell content. During the solvent charge, the valve V3 is kept open to remove residual CO<sub>2</sub> from the cell. This procedure generates a target composition of the polystyrene solution in pure toluene. The system is heated up and pressurized, and density and viscosity of the solution are measured at desired temperatures and pressures. After the measurement is completed, the system is brought back to ambient temperature and pressure. Then a known mass of CO<sub>2</sub> is injected to the system in addition to the polymer solution, resulting in a ternary mixture of polystyrene + toluene + CO<sub>2</sub>. Carbon dioxide is loaded from a high-pressure chamber whose weight is measured before and after the loading, so that the charged amount of CO<sub>2</sub> can readily be determined. After the measurement of density and viscosity of the ternary mixture at various temperatures and pressures, the system is brought to room temperature. A known amount of CO<sub>2</sub> is again added to the system, and the measurements are repeated.

The density of the solution is determined from the position of a piston from which the volume of the cell content at a given temperature and pressure can be calculated. The viscosity is determined by measuring the fall time of the sinker passing through the three LVDT coils. Viscosity  $\mu$  is related to the fall time  $t$ , the density of the sinker  $\rho_s$ , the density of the solution,  $\rho$ , and the instrument calibration constant  $K$  through  $\mu = K(\rho_s - \rho)t$ . The value of  $K$  has been previously determined by measuring the fall time of fluids of known viscosity and density.<sup>13</sup> The system temperature and pressure is controlled with an accuracy of  $\pm 0.1$  K and  $\pm 0.06$  MPa, respectively. The fall time is recorded with an accuracy of  $\pm 0.2$  ms, and the volume displacement of piston is measured with a  $\pm 0.2\%$  accuracy.

## RESULTS AND DISCUSSION

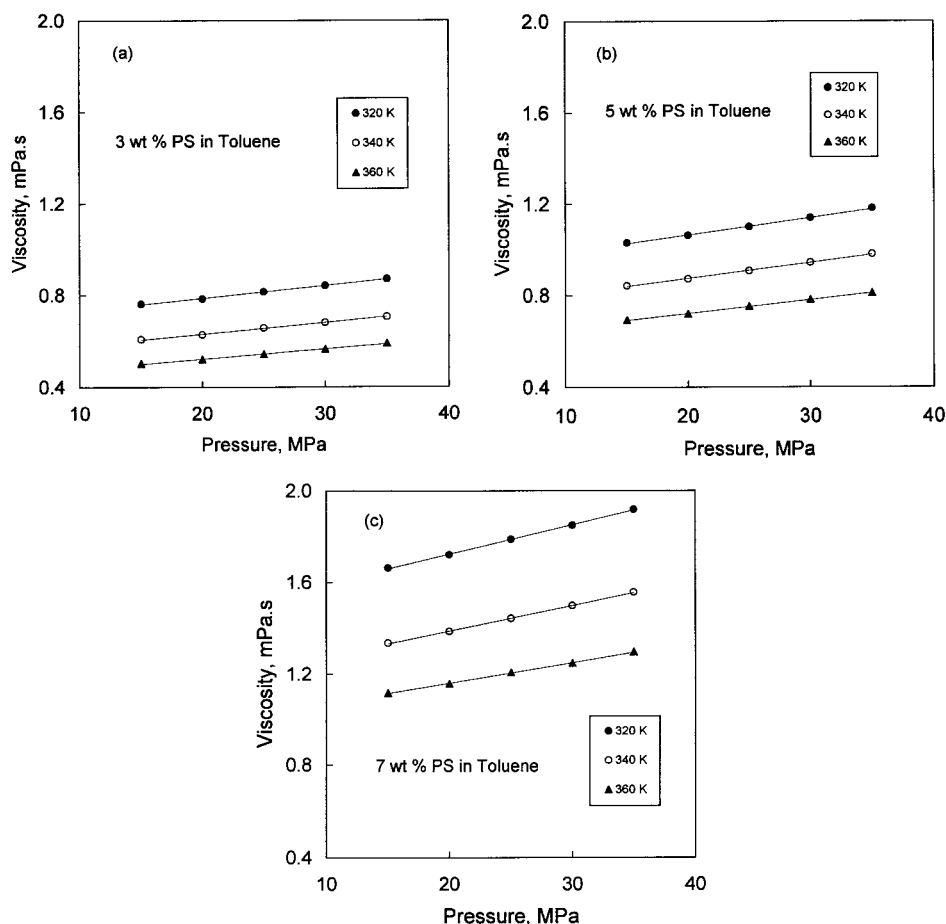
Viscosity data were obtained for solutions of polystyrene in toluene at polymer concentrations of the 3, 5, and 7 wt %. The concentration of CO<sub>2</sub> in the polymer + toluene + CO<sub>2</sub> mixtures was in the range 0–14.7 wt %. The density and viscosity measurements were carried out at temperatures of 320, 340, and 360 K, and at pressures of 15, 20, 25, 30, and 35 MPa.

### Polystyrene + Toluene System

Figure 2(a)–(c) shows the viscosity of polystyrene solutions in pure toluene as a function of temperature and pressure at concentration of 3, 5, and 7 wt %, respectively. The viscosity varied linearly with pressure at the temperatures and concentrations investigated. The viscosity of the solution was higher than the viscosity of the identical polymer in methylcyclohexane<sup>14</sup> at the same concentrations, which suggests greater chain extension of the polymer in toluene. The pressure dependency of viscosity is often explained through the equation<sup>15</sup>  $\eta = A \exp(V^\# P/RT)$  where  $\eta$  is viscosity,  $A$  a constant,  $V^\#$  the flow activation volume,  $P$  the pressure,  $R$  the gas constant, and  $T$  is the temperature. The flow activation volumes that have been determined are shown in Table I. The activation volumes show an increase with temperature or polymer concentration. The values are similar to the activation volumes that were observed in other solutions of polystyrenes in hexane and methylcyclohexane<sup>14,16</sup>

The temperature effect on viscosity can be described by the equation  $\eta = A \exp(E/RT)$ , where  $A$  is a constant and  $E$  is the flow activation energy. The activation energies of the solutions were calculated at each pressure and concentration, and are summarized in Table I. The result shows that the activation energy is about 9 kJ/mol, and is practically independent of pressure and polymer concentration at the experimental conditions investigated. For comparison, it may be noted that the activation energies were in the range of 7.1–10.0 in polystyrene solutions in methylcyclohexane<sup>14</sup> at the same conditions.

The viscosity of the solutions correlate with the density of the solutions, as shown in Figure 3. The plot includes the density and viscosity for pure toluene for comparisons. The present data for pure toluene compare well with the literature values<sup>17</sup> within a 2.8% accuracy. The data corre-

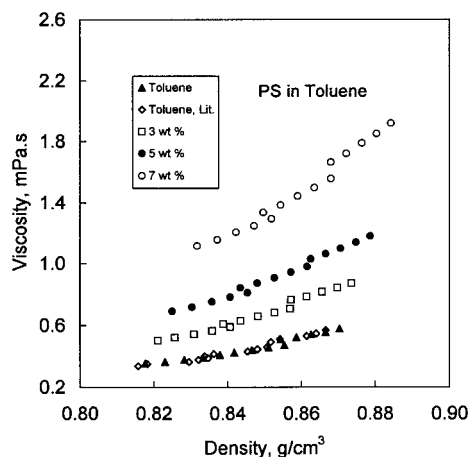


**Figure 2** Variation of viscosity of polystyrene solutions in toluene with pressure at 320, 340, and 360 K with the polystyrene concentrations of (a) 3 wt %, (b) 5 wt %, and (c) 7 wt %.

spond to a temperature range of 320–360 K and a pressure range of 15–35 MPa. For each concentration, the viscosity data at various pressures and temperatures essentially collapse into a single curve when plotted as a function of density. Even though some temperature-dependent variations are noted and they may become more apparent at high polymer concentrations, the viscosity–density data in Figure 3 were correlated using a Doolittle-type equation<sup>18</sup>  $\eta = A \exp\{B/(1 - V_0\rho)\}$  where  $A$  and  $B$  are constants,  $\rho$  is the density, and  $V_0$  is the closed-packed volume. The closed-packed volumes of the solutions at different concentrations were then calculated using a nonlinear regression method. The estimated closed-packed volumes for the 0, 3, 5, and 7 wt % solutions are shown in Table II. These values are somewhat lower than the values for the polystyrene solutions in methylcyclohexane (0.67–0.68 cm<sup>3</sup>/g) at the same concentrations,<sup>14</sup> which may

**Table I** Activation Volume  $V^\#$  (cm<sup>3</sup>/mol) and Activation Energy  $E$  (kJ/mol) for Polystyrene Solutions in Toluene at Polymer Concentrations of 0, 3, 5, and 7 wt %

$T$ (K)	Activation Volume $V^\#$ (cm <sup>3</sup> /mol)				
	Polymer Concentration				
	0 wt %	3 wt %	5 wt %	7 wt %	
320	16.76	17.82	18.09	19.15	
340	19.50	21.48	21.76	21.77	
360	20.35	23.94	23.95	22.45	
$P$ (MPa)	Activation Energy $E$ (kJ/mol)				
	15	8.71	9.93	9.52	9.53
	20	8.62	9.74	9.35	9.50
	25	8.57	9.67	9.10	9.41
	30	8.48	9.49	9.00	9.42
	35	8.45	9.24	8.99	9.38

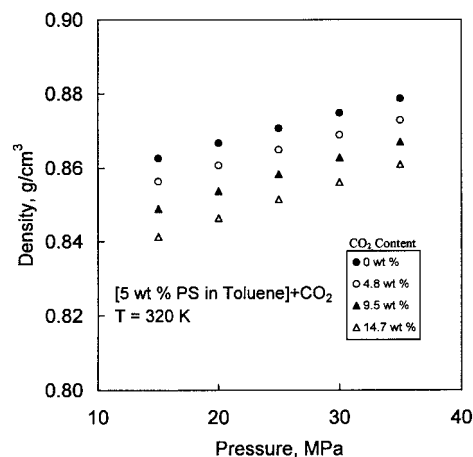


**Figure 3** Variation of viscosity of polystyrene solutions in toluene with density at the polymer concentrations of 0, 3, 5, and 7 wt %. Literature data from ref. 17.

be taken as indicating a more efficient packing in better solvent.

#### Polystyrene + Toluene + CO<sub>2</sub> System

Figure 4 shows a variation of density with pressure in polystyrene solution as a function of CO<sub>2</sub> concentration in the polystyrene + toluene + CO<sub>2</sub> mixture. The data correspond to the base solution of 5 wt % polystyrene in pure toluene, and to those solutions obtained by subsequent additions of CO<sub>2</sub> into this mixture. Density of the polymer solutions in pure toluene as well as in toluene + CO<sub>2</sub> mixtures exhibits a linear increase with increasing pressure at a given temperature at the CO<sub>2</sub> concentrations investigated. As shown in the figure, the density of the solution decreases as CO<sub>2</sub> concentration is increased. At a constant pressure and temperature, the density decrease was nearly proportional to the CO<sub>2</sub> concentration in the solution. Figure 5 shows the density variation of a typical solution as a function of pressure at different temperatures. As expected, the density decreases with temperature.

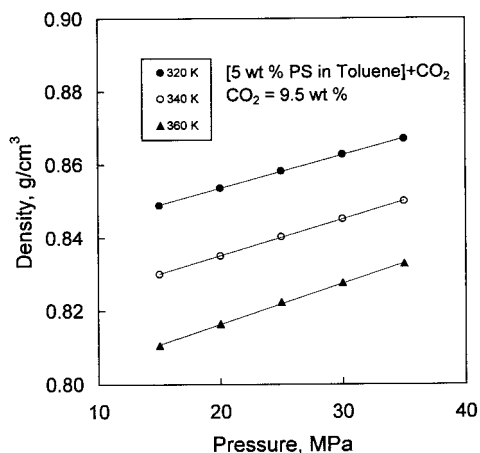


**Figure 4** Variation of density of [5 wt % polystyrene solution in toluene] + CO<sub>2</sub> mixtures with pressure at 320 K. Legend represents the CO<sub>2</sub> concentration in the mixture.

Figure 6(a)–(c) shows the viscosity variation for base solutions of 3, 5, and 7 wt % polystyrene in toluene upon addition of various levels of CO<sub>2</sub>. The data were obtained as a function of pressures at a constant temperature of 320 K. The viscosity of the polymer solutions in pure toluene and in toluene + CO<sub>2</sub> mixtures both exhibit the linear variation with pressure in the pressure range investigated. At a constant pressure, the viscosity of the polymer solutions decreased as CO<sub>2</sub> concentration increased. At the same CO<sub>2</sub> addition level, the reduction in viscosity was observed to be greater in solutions of higher polymer concentration. Figure 7(a)–(c) shows the viscosity variation of the 3, 5, and 7 wt % polymer solutions at 360 K. Compared to the data of 320 K, the viscosity reductions were lower at the same CO<sub>2</sub> content for each polymer concentration. Similar observations on temperature effect have been reported in connection with viscosity reduction of a polymer melt upon addition of carbon dioxide.<sup>10,11</sup> In the case of polymer melts, the diminishing viscosity reduc-

**Table II** Parameters of the Doolittle Type Equation  $\eta = A \exp\{B/(1 - V_0\rho)\}$  for Density Dependence of Viscosity of Polystyrene Solutions in Toluene at Polymer Concentrations of 0, 3, 5, and 7 wt %

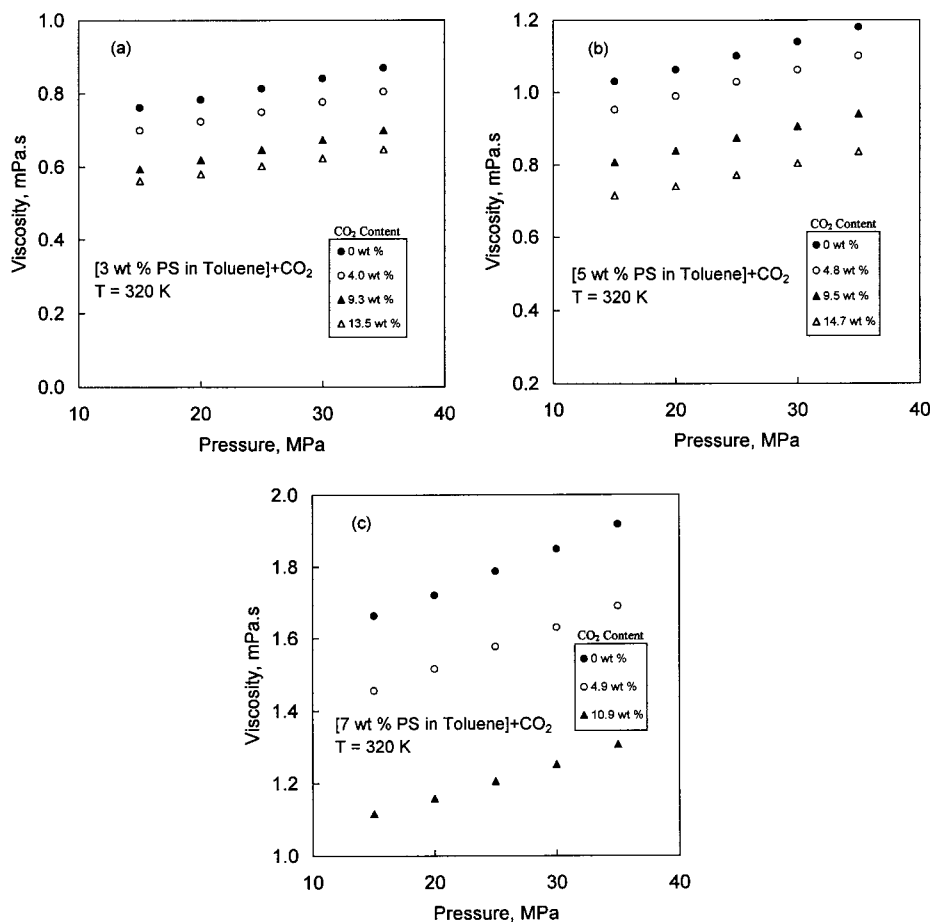
Polymer Conc.	A	B	V <sub>0</sub> (g/cm <sup>3</sup> )	Coefficient of Determination
0 wt %	0.0001086	4.128	0.596	0.9982
3 wt %	0.0001058	4.292	0.601	0.9972
5 wt %	0.0001162	4.283	0.611	0.9953
7 wt %	0.0001342	4.275	0.627	0.9945



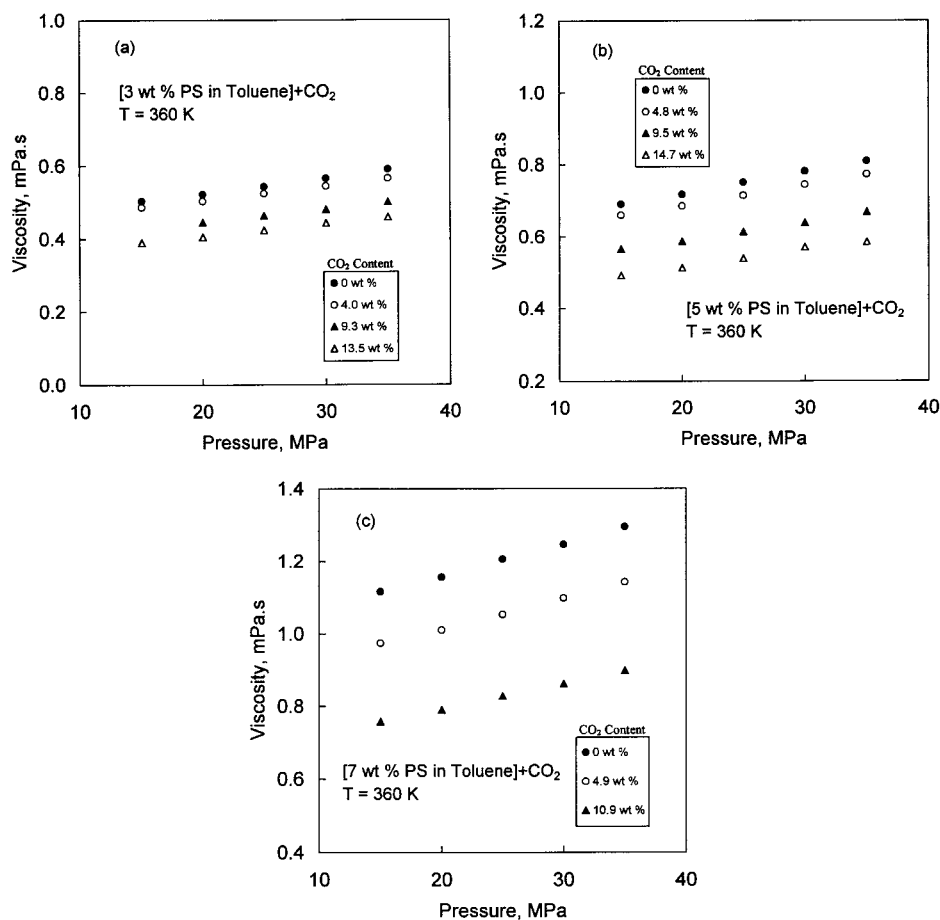
**Figure 5** Variation of density of [5 wt % polystyrene solution in toluene] + CO<sub>2</sub> mixtures with pressure at 320, 340, and 360 K. Carbon dioxide concentration in the mixture is 9.5 wt %.

tion at elevated temperatures is known to be due, in part, to the decrease in the solubility of CO<sub>2</sub> in the polymer. This is not the case in the present study. In the present system, the viscosity of the polymer solutions at the same CO<sub>2</sub> concentrations have been measured at different temperatures, while they are still completely miscible. Here the base viscosity of the solutions is reduced as temperature is increased, and the present result indicates that addition of CO<sub>2</sub> does not lead to further significant reductions in viscosity.

Figure 8 shows the temperature effect on the viscosity of a 5 wt % polystyrene solution in a typical mixed solvent. As expected, the viscosity decreases with increasing temperature. The solutions at all polymer and CO<sub>2</sub> concentrations investigated exhibit a linear variation of viscosity with pressure at these temperatures. This behavior is similar to the behavior of the poly-



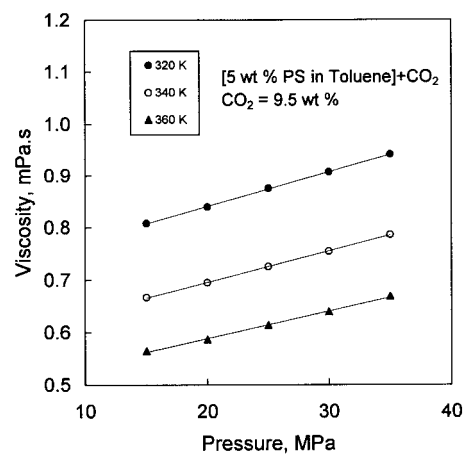
**Figure 6** Variation of viscosity of polystyrene solutions in toluene + CO<sub>2</sub> mixtures with pressure at 320 K. Base solution is (a) [3 wt % polystyrene in toluene] + CO<sub>2</sub>; (b) [5 wt % polystyrene in toluene] + CO<sub>2</sub>; (c) [7 wt % polystyrene in toluene] + CO<sub>2</sub>.



**Figure 7** Variation of viscosity of polystyrene solutions in toluene + CO<sub>2</sub> mixtures with pressure at 360 K. Base solution is (a) [3 wt % polystyrene in toluene] + CO<sub>2</sub>; (b) [5 wt % polystyrene in toluene] + CO<sub>2</sub>; (c) [7 wt % polystyrene in toluene] + CO<sub>2</sub>.

mer solutions in pure toluene. The flow activation volume and the activation energy for the 5 wt % polystyrene solutions in toluene were calculated at various CO<sub>2</sub> additions. The results are given in Table III. The activation volume appears to increase with CO<sub>2</sub> addition to the mixture. The activation energy is found to be essentially unchanged with the CO<sub>2</sub> addition levels investigated.

Figure 9(a)–(c) demonstrates the variation of viscosity as function of density for the 3, 5, and 7 wt % polystyrene solutions in toluene + CO<sub>2</sub> mixtures of various CO<sub>2</sub> concentrations. These data corresponds to temperatures of 320, 340, and 360 K, and to the pressure range of 15–35 MPa. The results show that the correlation of viscosity with density at different pressures and temperatures tends to collapse the data towards a single curve for the solutions in mixed solvents also. In these figures, the viscosity of solutions at different CO<sub>2</sub>



**Figure 8** Variation of viscosity of [5 wt % polystyrene solution in toluene] + CO<sub>2</sub> mixtures with pressure at 320, 340, and 360 K. Carbon dioxide concentration in the mixture is 9.5 wt %.

**Table III** Activation Volume  $V^\#$  ( $\text{cm}^3/\text{mol}$ ) and Activation Energy  $E$  ( $\text{kJ}/\text{mol}$ ) for [5 wt % Polystyrene in Toluene] +  $\text{CO}_2$  Mixtures at  $\text{CO}_2$  Concentrations of 4.8, 9.5, and 14.7 wt %

$T$ (K)	Activation Volume $V^\#$ ( $\text{cm}^3/\text{mol}$ )			
	CO <sub>2</sub> Content			
	0 wt %	4.8 wt %	9.5 wt %	14.7 wt %
320	18.09	18.89	20.21	21.28
340	21.76	19.78	23.17	22.04
360	23.95	23.64	25.44	27.23

$P$ (MPa)	Activation Energy $E$ ( $\text{kJ}/\text{mol}$ )			
	0 wt %	4.8 wt %	9.5 wt %	14.7 wt %
15	9.52	8.75	8.55	8.96
20	9.35	8.76	8.54	8.76
25	9.10	8.69	8.46	8.60
30	9.00	8.48	8.34	8.22
35	8.99	8.42	8.15	8.54

concentrations can be easily compared at the same density conditions. It was found that the polymer solutions of the same overall mixture density display different viscosities for different  $\text{CO}_2$  content in the mixtures. The viscosity of the polymer solutions decrease with  $\text{CO}_2$  content at the same overall mixture density. This observation was not as apparent at low polymer concentrations; however, it became clear as the polymer concentration increased. Therefore, contribution of the same amount of  $\text{CO}_2$  to the viscosity reduction in a polymer solution was found to be greater for solutions with a higher polymer concentration. For example, in the case of 3 wt % polymer solution, the viscosity was reduced by 7.6% (viscosity changed from 0.6288 to 0.5806 mPa(s) after addition of  $\text{CO}_2$  (13.5 wt %  $\text{CO}_2$ ) to the polymer solution in pure toluene when compared at the same constant density of  $0.847 \text{ g}/\text{cm}^3$  [Fig. 9(a)]. In the case of 7 wt % polymer solution, the viscosity dropped 23.7% [viscosity changed from 1.3360 to 1.0184 mPa(s)] when  $\text{CO}_2$  was added to a level of 10.9 wt %, also compared at the same density of  $0.847 \text{ g}/\text{cm}^3$  [Fig. 9(c)].

The correlation of density and viscosity in Figure 9(a)–(c) has been carried out employing the same Doolittle-type equation described in the previous sections for polystyrene + toluene solutions. The closed-packed volumes of the polystyrene solutions at different  $\text{CO}_2$  concen-

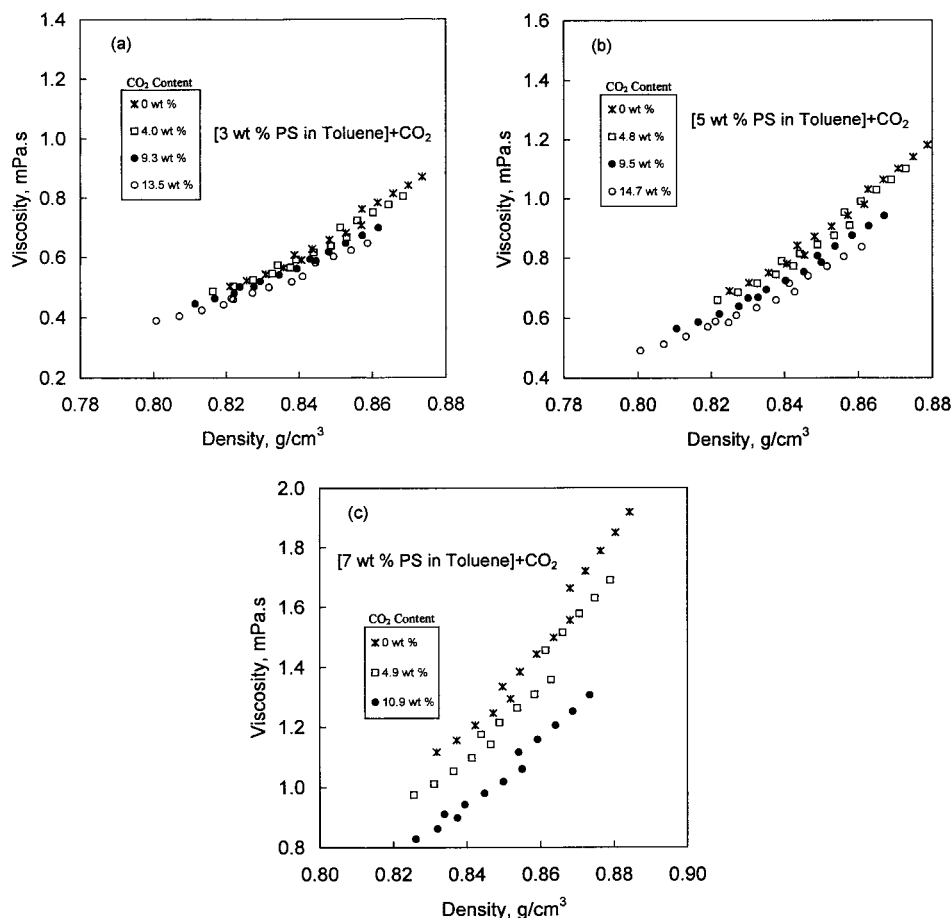
trations were estimated. It was found that the closed-packed volumes for the polymer solutions in pure toluene were essentially unchanged with the addition of  $\text{CO}_2$  within the  $\text{CO}_2$  concentration range investigated. Therefore, the estimated closed-packed volumes for solutions in pure toluene (Table II) are still applicable to the solutions in toluene +  $\text{CO}_2$  mixtures at each polymer concentration.

Figure 10 demonstrates the viscosity reduction as a function of  $\text{CO}_2$  concentration in the 3, 5, and 7 wt % polystyrene solutions. The data correspond to the constant pressure of 20 MPa and two temperatures, 320 and 360 K. The viscosity of pure  $\text{CO}_2$  included in the figure corresponds to data at 20 MPa and 340 K.<sup>19</sup> This plot illustrates the trends on the viscosity drop of the polymer solutions for  $\text{CO}_2$  addition levels below 20%. The figure shows that  $\text{CO}_2$  addition brings about the largest viscosity reduction in solutions of high polymer concentration at low temperatures for which the initial viscosities are relatively high.

In this study, we investigated the range of  $\text{CO}_2$  concentrations up to 14.7 wt % to maintain complete miscibility.<sup>12</sup> If the experiments were extended to higher  $\text{CO}_2$  concentrations, one would, in principle, expect merging of the viscosity data with that of  $\text{CO}_2$ . Realistically, however, as the  $\text{CO}_2$  concentration is increased, the polymer solution will undergo phase separation into polymer- and solvent-rich phases at certain elevated  $\text{CO}_2$  concentration under the experimental conditions of this study. This procedure corresponds to the batch type operation of the gas antisolvent process used for the polymer particle formation.<sup>5</sup> In this respect, the present results provide information on the change in viscosity of the polymer solutions up to the point where phase separation occurs during particle formation process.

The viscosity reduction that is observed upon addition of  $\text{CO}_2$  into the existing polymer solution could, in part, arise from the dilution of the original solution. The addition of  $\text{CO}_2$  without changing the amount of polymer and toluene inside the cell necessarily lowers the overall polymer concentration in the mixture, and hence, the viscosity should decrease accordingly. However, the viscosity of a polymer solution in a typical mixture of toluene +  $\text{CO}_2$  was lower than a polymer solution in the pure toluene solvent, which is at the same overall polymer concentration. An example of the numerical illustration is as follows. In Figure 6(b), 14.7

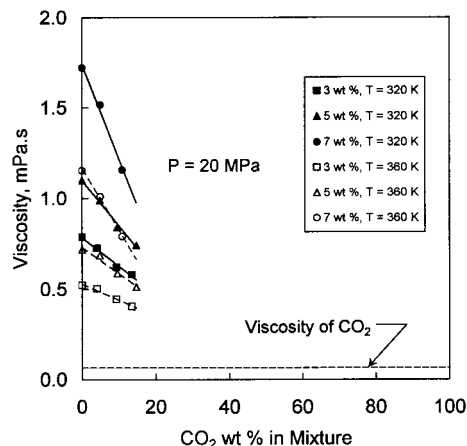




**Figure 9** Variation of viscosity of polystyrene solutions in toluene + CO<sub>2</sub> mixtures with density at various CO<sub>2</sub> concentrations. Base solution is (a) [3 wt % polystyrene in toluene] + CO<sub>2</sub>; (b) [5 wt % polystyrene in toluene] + CO<sub>2</sub>; (c) [7 wt % polystyrene in toluene] + CO<sub>2</sub>.

wt % CO<sub>2</sub> case corresponds to an overall polymer concentration in the polystyrene + toluene + CO<sub>2</sub> mixture of 4.2 wt %. The open triangular data points in Figure 6(b) correspond to this mixture with 4.2 wt % of polymer, 14.7 wt % CO<sub>2</sub>, and 81.1 wt % toluene at 320 K. The viscosity of this mixture was lower than the viscosity of 3 wt % polymer solution in pure toluene at the same temperature in Figure 2(a). These results show that the presence of CO<sub>2</sub> in the solution effectively lowers the viscosity.

In conclusion, the addition of CO<sub>2</sub> into the polystyrene solutions in toluene reduces the solution viscosity. The viscosity reduction increases with the amount of CO<sub>2</sub> addition. The largest reductions in viscosity are achieved at lower temperatures and for solutions with high polymer concentrations. The viscosity of the polymer solutions decreases with CO<sub>2</sub> concentration at the same overall density of the solutions.



**Figure 10** Variation of viscosity of polystyrene solutions in toluene + CO<sub>2</sub> mixtures as a function of CO<sub>2</sub> concentration in the mixture. Pressure is constant at 20 MPa, and temperatures at 320 and 360 K. Legend represents the polymer concentration in the base polystyrene solutions in toluene.

This research has been supported in part by a DuPont Educational Grant.

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