

# Viscosity of Polystyrene Solutions Expanded with Carbon Dioxide

Rachel E. Whittier,<sup>1</sup> Dawei Xu,<sup>1</sup> John H. van Zanten,<sup>1</sup> Douglas J. Kiserow,<sup>1,2</sup> George W. Roberts<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, North Carolina State University, Box 7905, Raleigh, North Carolina 27695-7905

<sup>2</sup>U.S. Army Research Office, P.O. Box 12211, Research Triangle Park, North Carolina 27709-2211

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**ABSTRACT:** The viscosity of solutions of polystyrene (PS) in decahydronaphthalene (DHN) was measured in the presence of carbon dioxide (CO<sub>2</sub>) with a moving-piston viscometer. The effects of the CO<sub>2</sub> pressure (0–21 MPa), polymer concentration (1–15 wt %), temperature (306–423 K), and polymer molecular weight (126 and 412 kDa) on the viscosity were investigated. In the absence of CO<sub>2</sub>, the increase in the viscosity with increasing polymer concentration was approximately exponential in concentration and was well described by the Martin equation. All the data fell on a single line when the relative viscosity was plotted against  $cM^{0.50}$  (where  $c$  is the concentration of the polymer in solution and  $M$  is the molecular weight of the polymer). The viscosity of the polymer solution decreased with increasing

CO<sub>2</sub> pressure under otherwise constant conditions. For a given CO<sub>2</sub> pressure, the viscosity reduction was greatest when the relative viscosity was high in the absence of CO<sub>2</sub>, that is, for high-molecular-weight polymer, high polymer concentrations, and low temperatures. Reductions in the relative viscosity of almost 2 orders of magnitude were observed in some cases. The viscosity of solutions of PS in DHN also was measured in the presence of sulfur hexafluoride (SF<sub>6</sub>). At a given pressure, SF<sub>6</sub> was about as effective as CO<sub>2</sub> in reducing the solution viscosity. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 540–549, 2006

**Key words:** carbon dioxide; decahydronaphthalene polystyrene; solution properties; viscosity

## INTRODUCTION

The high viscosity of polymer solutions can be a significant barrier to their further processing. One example occurs in the hydrogenation of unsaturated polymers. The hydrogenation of commercial polymers can improve their properties<sup>1</sup> and can give rise to new materials that are difficult to synthesize from the corresponding monomers.<sup>2–4</sup> However, the kinetics of polymer hydrogenations with heterogeneous catalysts can be limited by the mass transport of both H<sub>2</sub> and polymer to and within the catalyst particles, especially at high polymer concentrations.<sup>5,6</sup>

Improved mass transport of both polymer and H<sub>2</sub> in hydrogenation reactions can be achieved by reduction of the viscosity of the polymer solution, which can be accomplished through the addition of carbon dioxide (CO<sub>2</sub>).<sup>7–9</sup> CO<sub>2</sub> is very soluble in many organic solvents and is environmentally benign, relatively inexpensive, easily recycled, and nontoxic in comparison with most

organic solvents. These factors, along with its low critical temperature (31°C), make CO<sub>2</sub> an ideal processing aid. Recently, so-called CO<sub>2</sub>-expanded organic solvents have received attention as reaction media for the oxidation of small molecules.<sup>10,11</sup> Hydrogenations of various organic liquids swollen with CO<sub>2</sub> also have been studied.<sup>12–14</sup> However, the use of CO<sub>2</sub>-expanded solvents for polymer hydrogenation is relatively unexplored,<sup>15</sup> despite the potential benefit associated with viscosity reduction. One problem is that CO<sub>2</sub> is an antisolvent for many polymers, causing the polymer to precipitate above some threshold pressure of CO<sub>2</sub>.<sup>9,15</sup>

To interpret the results of polymer hydrogenation experiments, the transport properties of solutions of the polymer being hydrogenated must be known. The hydrogenation of polystyrene (PS) to poly(cyclohexylethylene) is of significant interest,<sup>2,3,5,15,16</sup> and decahydronaphthalene (DHN) has been used as a solvent for this reaction.<sup>5,15</sup> Therefore, the viscosity of PS in DHN has been investigated over a range of conditions to aid in understanding PS hydrogenation kinetics.

The effect of the polymer concentration on the solution viscosity can be classified in one of three regimes: dilute, moderately concentrated, and concentrated.<sup>17</sup> The viscosity of moderately concentrated polymer solutions depends on the polymer concentration and molecular weight.<sup>17–19</sup> This work is focused

Correspondence to: G. W. Roberts (groberts@ncsu.edu).

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on the moderately concentrated regime, about 2–15 wt % PS, as this regime is of the greatest interest for PS hydrogenations.

Viscosity data are typically presented in dimensionless form, via the relative viscosity ( $\eta_r$ ) and the specific viscosity ( $\eta_{sp}$ ), as follows:

$$\eta_r = \frac{\eta}{\eta_s}$$

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s}$$

Here  $\eta$  is the viscosity of the polymer solution, and  $\eta_s$  is the viscosity of the solvent under identical conditions.

Gandhi and Williams<sup>18</sup> measured the viscosity of PS in several solvents, including DHN, at a single temperature, 25°C. They used polymer samples with a narrow molecular weight distribution; the polydispersity index (PDI) of both samples was less than 1.06. Gandhi and Williams found that  $\eta_r = f(cM_n^a)$  described the viscosity quite well. In this expression,  $c$  is the concentration of the polymer in solution, and  $M_n$  is the number-average molecular weight of the polymer. When the value of  $a$  was chosen properly, a plot of  $\eta_r$  versus  $cM_n^a$  collapsed the viscosity data for a given solvent onto a single curve independent of the polymer molecular weight and concentration. They found that  $a = 0.68$  for PS in thermodynamically good solvents such as toluene. For PS in DHN, they found  $a = 0.5$ . The value for  $a$  is thought to be indicative of the solvent power. A value of 0.5 is consistent with the fact that DHN is a  $\Theta$  solvent for PS under the experimental conditions of Gandhi and Williams.<sup>18</sup> Streeter and Boyer<sup>20</sup> also measured the viscosity of PS in DHN at 25°C. Their polymer had a weight-average molecular weight of 370,000. However, the molecular weight distribution was not characterized, and this makes a comparison with our data difficult. One feature of our research is that it extends this earlier work<sup>18,20</sup> to temperatures up to 150°C.

The viscosity of a polymer solution is known to decrease with the addition of CO<sub>2</sub>.<sup>7–9</sup> Yeo and Kiran<sup>8</sup> investigated the viscosity of 3–7 wt % PS ( $M_n = 50,000$ , PDI = 1.06) in toluene/CO<sub>2</sub> as a function of the polymer concentration, CO<sub>2</sub> concentration, and temperature. The viscosity decreased with increasing CO<sub>2</sub> concentration, with greater viscosity reductions for the higher polymer concentrations. The CO<sub>2</sub>-induced viscosity reduction also decreased with increasing temperature. Because CO<sub>2</sub> dissolves into the polymer solution in significant quantities, Yeo and Kiran investigated whether the viscosity reduction was due simply to the decrease in the polymer concentration. CO<sub>2</sub> reduced the viscosity to values lower than those expected strictly from a simple dilution of the polymer solution.

Li et al.<sup>9</sup> investigated dilute solutions (< ca. 1 wt %) of PS ( $M_n = 78,000$ , PDI = 1.1) in toluene at 35°C at CO<sub>2</sub> pressures up to 4.2 MPa. They found that the viscosity decreased approximately linearly with increasing CO<sub>2</sub> pressure. The viscosity depended on the CO<sub>2</sub> pressure to a greater degree in higher concentration solutions, presumably because CO<sub>2</sub> is an antisolvent for PS that reduces the favorability of interactions between the polymer and solvent. It was proposed that the solvent power of toluene/CO<sub>2</sub> mixtures decreased with increasing CO<sub>2</sub> pressure, and this increased the importance of polymer–polymer interactions and thereby reduced the entanglement density.

Wolf and Jend<sup>21</sup> measured the effect of pressure per se on the viscosity of PS in *trans*-DHN. They found that the viscosity increased with pressure up to the point of phase separation, which was in the region of 15–100 MPa. Although the effect of pressure depended on the temperature and polymer concentration, the viscosity was approximately exponential in pressure, with a coefficient of about  $8 \times 10^{-4} \text{ bar}^{-1}$ .

The objective of this research was to determine the effects of the temperature, polymer concentration, and CO<sub>2</sub> pressure on the viscosity of PS/DHN/CO<sub>2</sub> solutions. Investigations into the transport properties of this system should aid in our understanding of the kinetics of PS hydrogenation and should provide insight into the use of CO<sub>2</sub> to improve the transport properties of other polymer solutions.

## EXPERIMENTAL

### Materials

DHN (76% *trans*/24% *cis*) was purchased from Sigma–Aldrich (St. Louis, MO). Two different PS samples, with  $M_n$  values of 126,000 and 412,000, each having a PDI of 1.05, were purchased from Polymer Source, Inc (Montreal, Canada). The molecular weights were verified with intrinsic viscosity ( $[\eta]$ ) measurements and gel permeation chromatography.

### Viscometer operation

A Cambridge Applied Systems SPL 440 viscometer (Medford, MA) was used to measure the viscosity of PS in DHN and in DHN expanded with CO<sub>2</sub>. Magnetic coils on either end of the cylindrical measurement chamber applied an alternating magnetic force to move a piston back and forth in the fluid sample. The viscosity was calculated from the time required for the piston to move the length of the measurement chamber. The calculation was performed automatically by the SPL 440 software under the assumption that the fluid was Newtonian. The assumption of Newtonian behavior was checked by the measurement of the viscosity of two PS/DHN solutions at 33°C with a TA AR2000 stress-controlled rheometer

(TA Instruments, New Castle, DE). With these solutions, the viscosity was essentially independent of the shear rate over the range of shear rates at which the SPL 440 operated.<sup>22</sup> Pistons of three different diameters were used, as appropriate for the viscosity range of interest: 0.25–5, 5–100, and 50–1000 cp. A resistance temperature detector located at the bottom of the chamber measured the temperature of the sample. The viscometer was accurate to within 1% of the maximum of the measurement range (e.g., 1 cp for the 5–100-cp range). The shear rate was a function of the piston diameter and the fluid viscosity and could not be controlled with this viscometer. The shear rate varied inversely with the viscosity. With CO<sub>2</sub>, the shear rate generally was in the range of 1000–5000 s<sup>-1</sup>. Without CO<sub>2</sub>, the shear rate was generally lower, in the range of 300–1500 s<sup>-1</sup>.

The SPL 440 viscometer was installed in a mechanical convection oven for temperature control. The oven had a spatial uniformity of  $\pm 0.9^\circ\text{C}$  at 150°C. The viscosity was measured with each piston stroke. The reported data points represent an average of the results from the previous 20 piston cycles. The standard deviations of the sample temperature and viscosity were calculated automatically by the instrument. The viscosity was recorded when the standard deviation of the sample temperature was less than 0.1°C and the standard deviation of the viscosity was less than 1% of the average viscosity.

For polymer solutions expanded with CO<sub>2</sub>, the viscometer was connected to a high-pressure view cell so that the phase behavior of the polymer/solvent/CO<sub>2</sub> system could be monitored. The view cell and viscometer were filled with the polymer solution, and a headspace was left above the solution in the view cell. CO<sub>2</sub> was added to the system at a set pressure. The polymer/DHN/CO<sub>2</sub> solution was circulated through the viscometer with a manual pump for several minutes, and the system then was allowed to sit for at least 1 h. Viscosity measurements were performed over a range of CO<sub>2</sub> pressures. However, the polymer precipitated from solution once the CO<sub>2</sub> pressure exceeded some critical value, which depended on the temperature. The CO<sub>2</sub> pressure at which the polymer precipitated from solution was measured independently at each temperature.<sup>15</sup> All the viscosity data were obtained at CO<sub>2</sub> pressures below this critical value.

A Rheotek RPV-1 automated viscometer (La Grange, KY) was used to measure the  $[\eta]$  values of PS in DHN at 40°C for the  $M_n = 126,000$  sample and at 40 and 90°C for the  $M_n = 412,000$  sample.

## RESULTS AND DISCUSSION

### DHN viscosity

The viscosity of DHN was measured at 33, 60, 90, and 120°C. In Figure 1, the experimental results are com-

pared with literature values for the pure cis and trans isomers.<sup>23</sup> The experimental results lie between the curves for the two isomers over the whole temperature range. The data are quite close to the curve for *trans*-DHN, and this is consistent with the 76% trans/24% cis composition of the DHN used for this research.

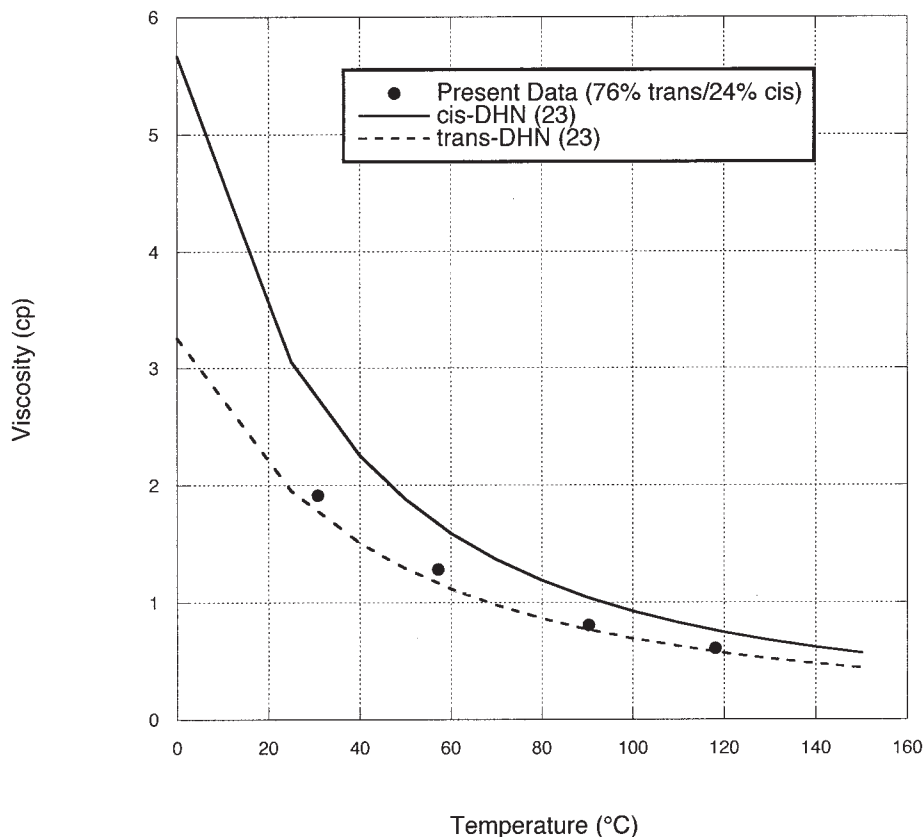
### PS–DHN viscosity

The viscosity of solutions of 2–15 wt % PS in DHN was measured for both polymer molecular weights from 33 to 150°C. This polymer concentration range corresponds to that used in studies of PS hydrogenation.

Figure 2 shows the relative viscosity of PS/DHN solutions (without CO<sub>2</sub>) at various temperatures and polymer concentrations. Several trends are evident. First, the addition of as little as 2 wt % polymer to the solvent significantly increased the solution viscosity. Second, at a given polymer concentration and temperature, the viscosity of the  $M_n = 412,000$  polymer solution was significantly higher than that of the  $M_n = 126,000$  solution, especially at high PS concentrations. At 15 wt % PS, the viscosity of the higher  $M_n$  solution was almost an order of magnitude higher than that of the lower  $M_n$  solution at a given temperature. The viscosity of the polymer solution decreased with increasing temperature. However, much of this viscosity decrease was explained by the decrease in the solvent viscosity with increasing temperature. Plotting the data as the relative viscosity ( $\eta_r$ ) brings the data at different temperatures quite close together in Figure 2.

The increase in the viscosity with the polymer concentration was approximately exponential, as indicated by the straight lines on Figure 2. These lines were fitted to all the data for a given molecular weight; that is, the effect of temperature was ignored. The slopes of the two lines indicate that the increase in  $\ln \eta_r$  with the polymer concentration was approximately 50% greater for the higher  $M_n$  polymer. Wolf and Jend<sup>21</sup> also found an exponential relationship between the viscosity and polymer concentration for PS in *trans*-DHN. However, their study used a single molecular weight and a single temperature.

Figure 3 is a test of the correlation proposed by Gandhi and Williams<sup>18</sup> for the viscosity of PS in DHN. Consistent with their results, all the data from this study fell on a single curve when  $\eta_r$  was plotted against  $c(M_n)^{0.5}$ , over the entire range of temperatures and concentrations, for both molecular weights. However, these data cover a range of temperature, whereas the original data of Gandhi and Williams were all at 25°C. Therefore, the Gandhi–Williams correlation may be more robust than originally anticipated. The ability of a single value of  $a$  to correlate the data over such a wide range of temperature is surprising. If  $a$  depends on the quality of the solvent, its value would be expected to vary with the temperature. Finally, the plot



**Figure 1** Measured viscosity of 76% *trans*-DHN/24% *cis*-DHN. The solid lines are literature values;<sup>23</sup> the filled circles are data from this study.

of  $\ln(\eta_r)$  versus  $cM_n^{0.5}$  in Figure 3 is almost linear. This is consistent with the exponential relationship between  $\eta_r$  and  $c$ , as pointed out in the discussion of Figure 2.

Figure 3 contains four points that were read from Figure 7 of Gandhi and Williams.<sup>18</sup> At low concentrations, these points agree reasonably well with our data. At higher concentrations, the viscosities measured by Gandhi and Williams appear to be higher than those measured in this study. The deviations might be due to the difficulty of accurately extracting values from Figure 7 of Gandhi and Williams. They also may be due to some viscosity reduction due to shear thinning in this study. However, independent measurements<sup>22,24</sup> suggest that shear thinning is not significant at 25°C at the high polymer concentrations at which the deviations are most significant.

The data of Streeter and Boyer<sup>20</sup> agreed reasonably well with our data. However, an exact comparison was not possible for the reasons stated earlier.

For moderate polymer concentrations, the Martin equation, shown next, has been found to describe the effect of the polymer concentration on the viscosity:

$$\ln\left(\frac{\eta_{sp}}{c[\eta]}\right) = k(c[\eta])$$

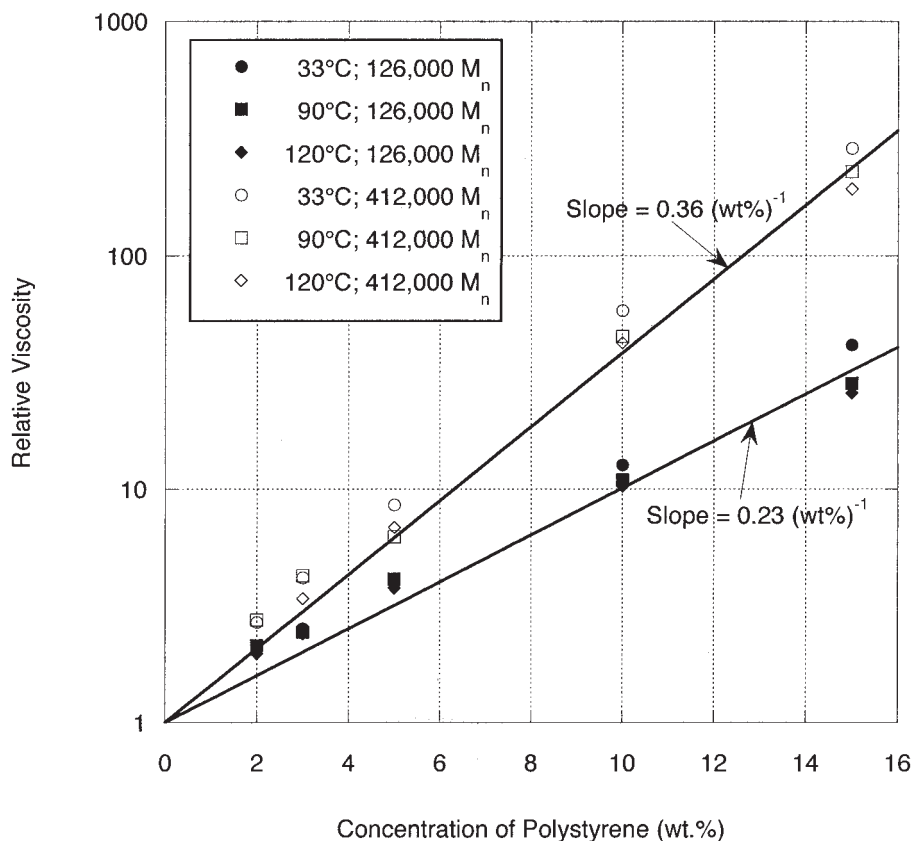
In this equation,  $c$  is the concentration of the polymer and  $k$  is a constant of proportionality. With measured

$[\eta]$  values at 40 and 90°C, the experimental data were tested against this equation, as shown in Figure 4. At fixed values of the temperature and  $M_n$ , the Martin equation provides a satisfactory description of the increase in the viscosity with the polymer concentration. However, the data are scattered at low polymer concentrations for the low-molecular-weight polymer at 40°C.

The dimensionless concentration ( $c[\eta]$ ) indicates the concentration regime of the polymer solution.<sup>25</sup> The semidilute (coil overlap) region, where the polymer chains begin to overlap, occurs in the range of  $1 < c[\eta] < 10$ . At higher values of  $c[\eta]$ , the concentration is in the entangled regime, where interactions between polymer molecules contribute significantly to the viscosity.<sup>26</sup> From Figure 4, the range of  $c[\eta]$  covered by this research is in the semidilute region, not the entangled regime, at least at 40 and 90°C.

The slope ( $k$ ) of the lines in Figure 4 is thought to be indicative of the solvent quality, with a smaller  $k$  value indicating a thermodynamically better solvent.<sup>26</sup> The values of  $k$  at 40°C for the two molecular weights are similar, although the difference is statistically significant. The value of  $k$  for the  $M_n = 412,000$  polymer at 40°C is greater than the value at 90°C. This behavior is consistent with the interpretation of  $k$  as an index of the solvent quality. The solvent quality would be expected to decrease with





**Figure 2** Relative viscosity of PS in DHN at various polymer concentrations for two PS molecular weights and three temperatures. The relative viscosity is approximately exponential in concentration. The effect of temperature is relatively small.

decreasing temperature and be less sensitive to the molecular weight.

### Solubility of CO<sub>2</sub> in DHN

The solubility of CO<sub>2</sub> in DHN varies with the temperature and pressure. To understand the effect of CO<sub>2</sub> on the viscosity over a range of conditions, it is necessary to know the molar fraction of CO<sub>2</sub> dissolved in the liquid phase. The Peng–Robinson equation of state was used to estimate the amount of CO<sub>2</sub> in *trans*-DHN at each experimental condition. PS was not taken into account in these calculations. Its effect on the CO<sub>2</sub> solubility was assumed to be negligible for the polymer concentrations used in this work. The binary interaction parameter ( $k_{ij}$ ) in the Peng–Robinson equation of state was determined to be 0.125 by the matching of the calculated CO<sub>2</sub> solubility data to equilibrium data.<sup>15</sup>

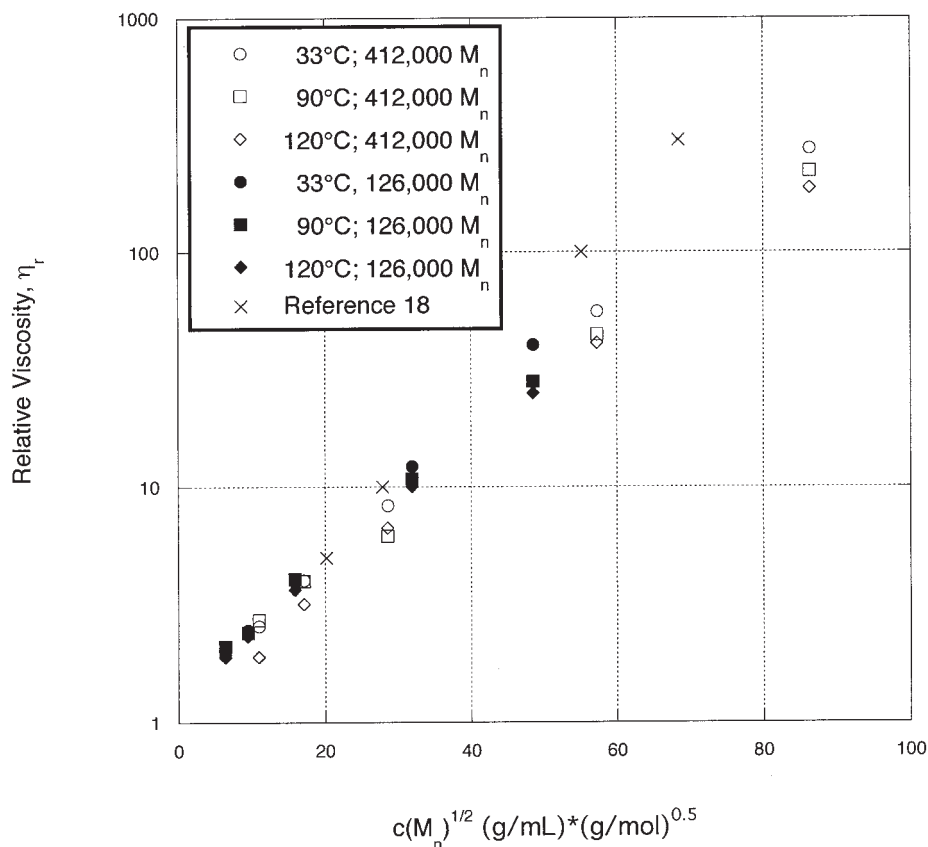
Figure 5 shows the calculated solubilities for the range of pressures and temperatures covered in this research. Substantial amounts of CO<sub>2</sub> were dissolved in DHN under the conditions of this study. The dotted lines and arrows illustrate that, at a constant pressure, the solubility of CO<sub>2</sub> in DHN decreased substantially with increasing temperature. For example, at 5.5 MPa

CO<sub>2</sub>, the molar fraction of CO<sub>2</sub> in the liquid phase decreased from 0.53 at 33°C to 0.21 at 150°C.

### PS–DHN–CO<sub>2</sub> viscosity

The viscosity of 1, 3, 8.5, 10, and 12.5 wt % PS in DHN was measured at 33, 90, and 150°C at various pressures of CO<sub>2</sub> and with both polymer molecular weights. The maximum CO<sub>2</sub> pressure at each temperature was 6.9, 13.8, and 20.7 MPa, respectively. These upper pressure bounds were determined by the tendency of CO<sub>2</sub> to act as an antisolvent for PS, causing the polymer to precipitate. These pressures were just below the threshold pressure at which precipitation occurred.

The solution viscosity was reduced significantly by the addition of CO<sub>2</sub>. Figure 6 shows the relative viscosity at several PS concentrations over a range of CO<sub>2</sub> pressures for the  $M_n = 412,000$  polymer at 90°C. The PS concentrations are the initial solution concentrations before the addition of CO<sub>2</sub>. The estimated weight fraction of CO<sub>2</sub> in *trans*-DHN under these conditions is shown on the top axis of Figure 6. The relative viscosities in the presence of CO<sub>2</sub> were calculated by the division of the viscosity of the polymer solution by the viscosity of DHN at the same temperature and CO<sub>2</sub>



**Figure 3** Relative viscosity of PS in DHN with the Gandhi–Williams correlation<sup>18</sup> to describe the effects of  $M_n$  and  $c$ .

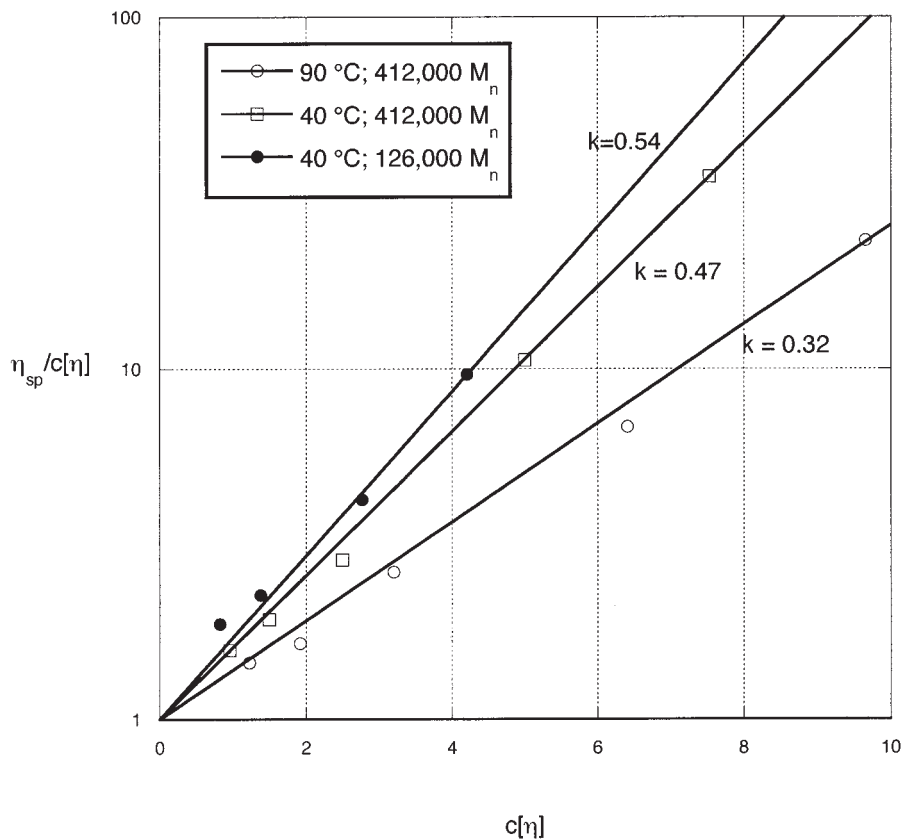
pressure. Thus, these relative viscosities account for the effects of both the temperature and  $\text{CO}_2$  pressure on the solvent viscosity. This figure is representative of the viscosity decrease seen for both PS molecular weights over the range of temperatures studied.

For both molecular weights, the difference in the relative viscosity between a solution with no  $\text{CO}_2$  pressure applied and a solution with the maximum  $\text{CO}_2$  pressure applied increased with increasing PS concentration. In other words, the application of  $\text{CO}_2$  pressure was more effective in reducing the solution viscosity when the polymer concentration was high. This result is consistent with the work of others.<sup>7,8</sup> At increasing PS concentrations, polymer chains become more overlapped. In DHN, the PS chains are nearing the start of the entanglement regime at about 10 wt % PS.  $\text{CO}_2$  reduces the solvent quality and causes the chains to contract. This is consistent with the fact that  $\text{CO}_2$  acts as an antisolvent for PS, eventually leading to polymer precipitation. The resulting viscosity reduction due to the decreased favorability of polymer–solvent interactions is more dramatic for the higher polymer concentrations, at which chains are highly overlapped in the absence of  $\text{CO}_2$ . As an aside, some of the scatter in the data, especially at high  $\text{CO}_2$  pressures, may be caused by the need to interpolate between  $\text{CO}_2$  pressures to estimate the solvent viscosity,

which is required to calculate  $\eta_r$ . Finally, the effect of adding  $\text{CO}_2$  to the PS solution clearly is more important than the effect of pressure per se. The work of Wolf and Jend<sup>21</sup> suggests that the viscosity should have increased by about 10% at the highest pressures in Figure 6, in comparison with the substantial decreases that were actually observed.

Figure 7 compares the effect of  $\text{CO}_2$  on the absolute viscosity of the  $M_n = 412,000$  polymer solution with its effect on the viscosity of the  $M_n = 126,000$  polymer solution. The polymer concentration, 8.5 wt %, and the temperature,  $90^\circ\text{C}$ , were constant for this figure. In the absence of  $\text{CO}_2$ , the  $M_n = 412,000$  polymer solution had a much higher viscosity than the  $M_n = 126,000$  solution. However, with the application of approximately 5.5 MPa  $\text{CO}_2$  (ca. 30 mol %  $\text{CO}_2$  in solution), the viscosities of both samples became comparable, at about 3–4 cP. As the  $\text{CO}_2$  pressure was increased further, the viscosity decrease of both solutions was relatively modest. At 14 MPa, the viscosity of both polymer solutions was roughly comparable to the viscosity of the solvent at the same temperature, in the absence of  $\text{CO}_2$ .

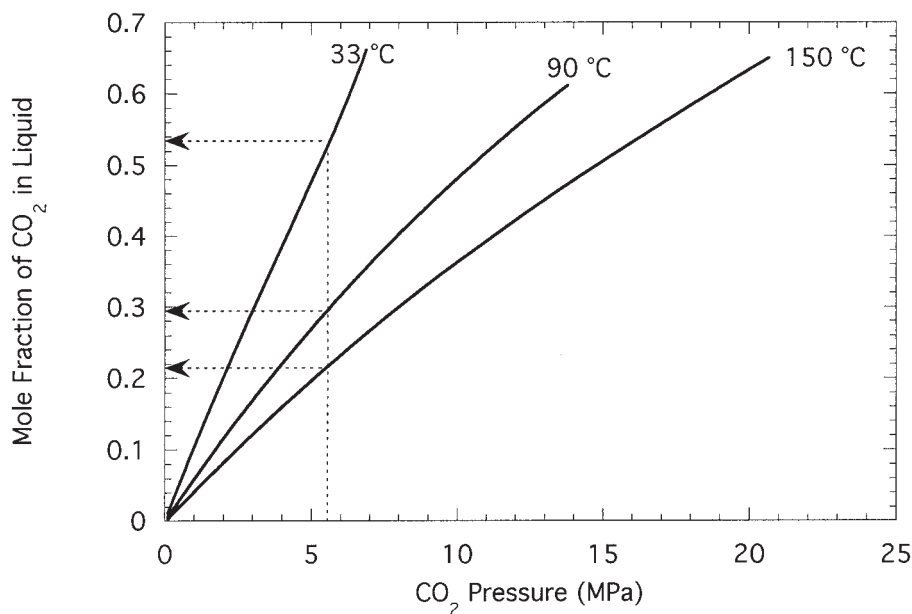
Figure 8 shows the viscosity of a 8.5 wt % solution of the  $M_n = 126,000$  polymer for several temperatures over a range of  $\text{CO}_2$  pressures. The viscosity reduction was greatest at the lowest temperature. As shown in



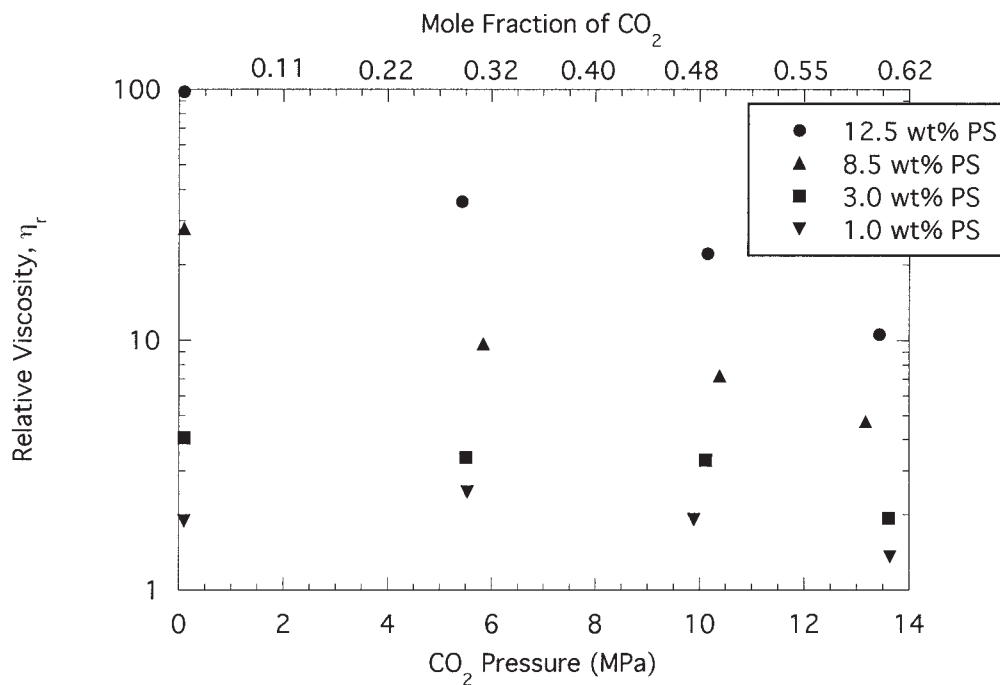
**Figure 4** Test of the Martin equation for PS in DHN at 40 and 90°C and for two PS molecular weights.

Figure 5, the  $\text{CO}_2$  solubility in DHN decreased with increasing temperature. Therefore, at a fixed  $\text{CO}_2$  pressure, the effect of  $\text{CO}_2$  was diminished at higher temperatures because less  $\text{CO}_2$  was dissolved in the solu-

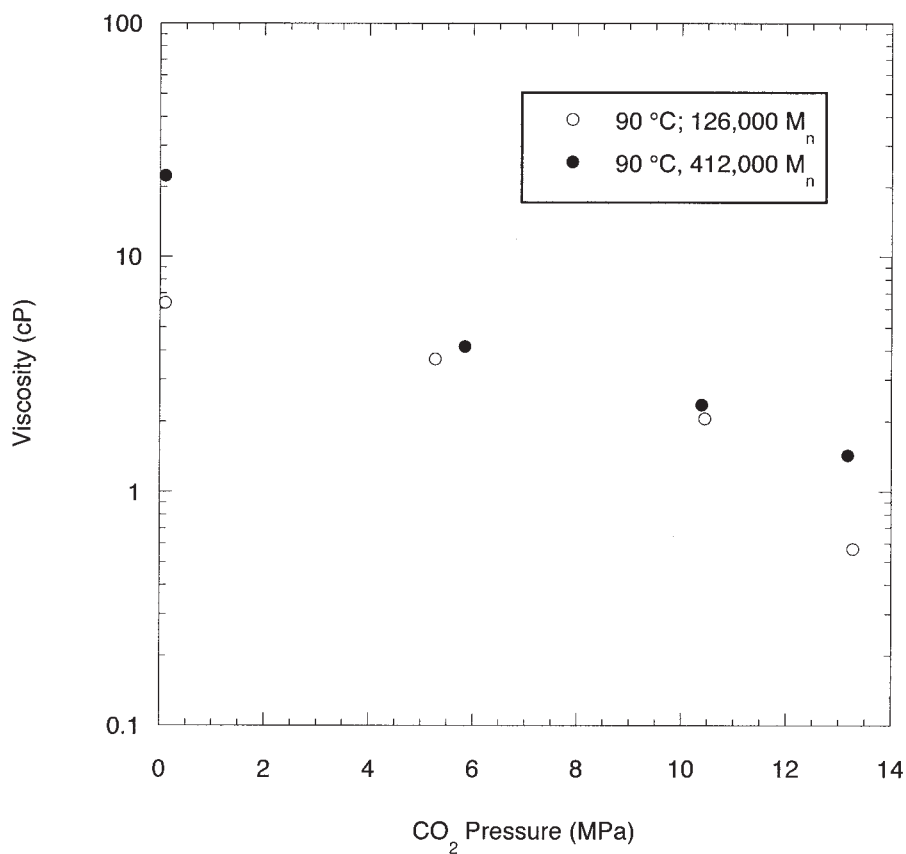
tion. However, at higher temperatures, higher pressures of  $\text{CO}_2$  could be applied before PS precipitated. At 150°C and 20 MPa  $\text{CO}_2$ , the viscosity of the 8.5 wt % solution was comparable to that of the pure solvent



**Figure 5** Solubility of  $\text{CO}_2$  in DHN calculated with the Peng–Robinson equation of state with  $k_{ij} = 0.125$ .<sup>15</sup> The dotted lines and arrows illustrate the decreasing solubility of  $\text{CO}_2$  with increasing temperature at a fixed pressure.

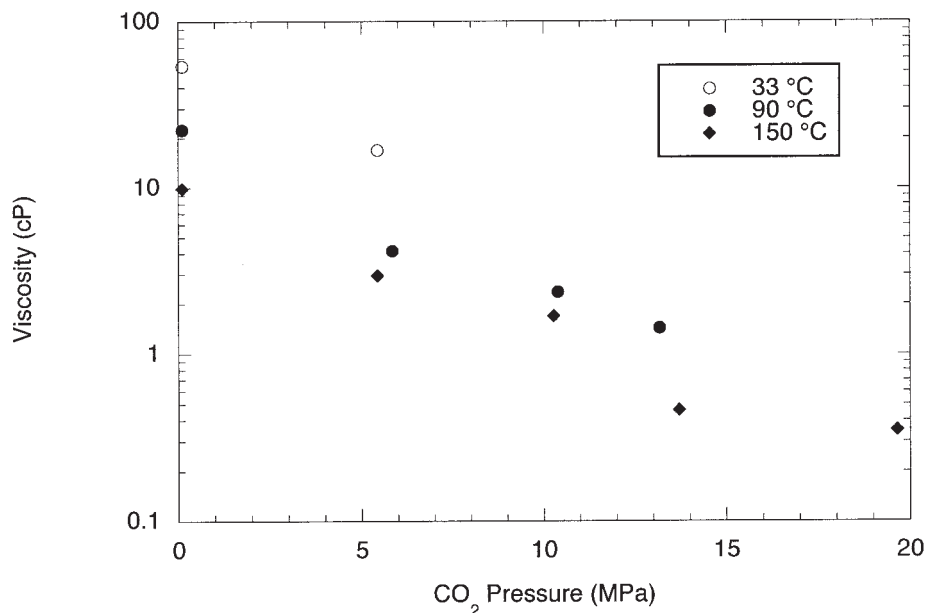


**Figure 6** Dependence of the relative viscosity of PS/DHN/CO<sub>2</sub> solutions on the CO<sub>2</sub> pressure ( $M_n = 412,000$ , 90°C). The polymer concentrations are those before the application of CO<sub>2</sub>.



**Figure 7** Relative viscosity of PS/DHN/CO<sub>2</sub> solutions as a function of the CO<sub>2</sub> pressure ( $M_n = 126,000$  and 412,000, 90°C). The polymer concentration was 8.5 wt % in DHN before the application of CO<sub>2</sub>.





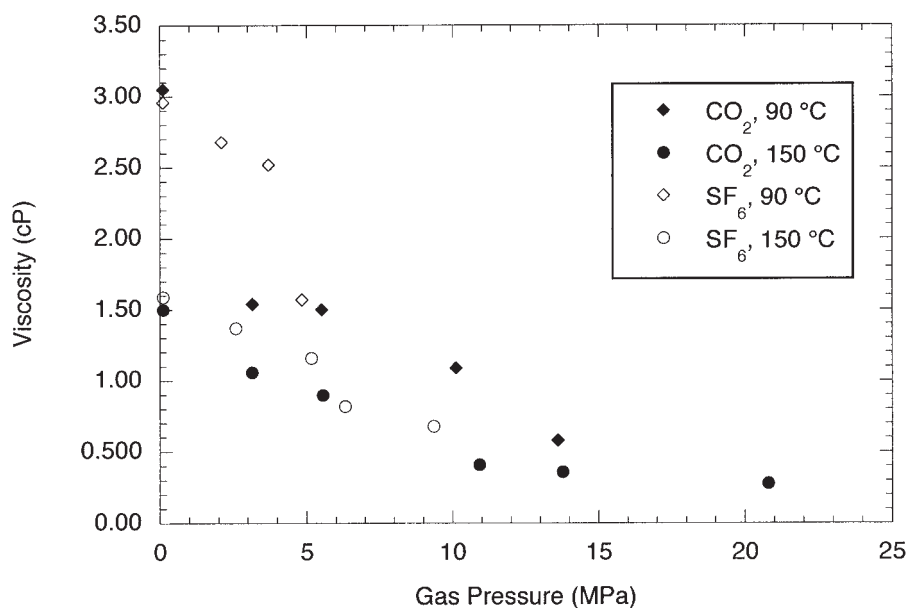
**Figure 8** Viscosity of PS/DHN/CO<sub>2</sub> solutions as a function of the CO<sub>2</sub> pressure at different temperatures (8.5 wt % PS in DHN before the application of CO<sub>2</sub>,  $M_n = 126,000$ ).

at the same temperature. However, at 33°C and the maximum permissible CO<sub>2</sub> pressure of 5.5 MPa, the viscosity of an 8.5 wt % solution was still about a factor of 8 greater than the solvent viscosity at the same temperature.

#### PS–DHN–sulfur hexafluoride (SF<sub>6</sub>) viscosity

The effect of SF<sub>6</sub> on the viscosity of PS/DHN solutions was measured to evaluate the uniqueness of the vis-

cosity reduction with CO<sub>2</sub>. SF<sub>6</sub> is a gas whose critical properties are similar to those of CO<sub>2</sub> (SF<sub>6</sub>, critical temperature = 46°C, critical pressure = 3.7 MPa; CO<sub>2</sub>, critical temperature = 31°C, critical pressure = 7.3 MPa). The viscosity of a 3 wt % solution of the  $M_n = 412,000$  polymer in DHN was measured at 90 and 150°C at various pressures of SF<sub>6</sub>. Figure 9 shows that, at a fixed pressure and temperature, the viscosity reduction with SF<sub>6</sub> was roughly comparable to that with CO<sub>2</sub>.



**Figure 9** Viscosity reduction with CO<sub>2</sub> and SF<sub>6</sub> as a function of the gas pressure (3 wt % PS in DHN before the application of gas pressure,  $M_n = 412,000$ ).

The SF<sub>6</sub> pressures in Figure 9 were chosen in an attempt to achieve the same range of molar fractions of SF<sub>6</sub> in DHN as of CO<sub>2</sub>. The solubility of SF<sub>6</sub> in DHN was calculated with the Peng–Robinson equation of state. However, no data on the SF<sub>6</sub>/DHN system could be found that would permit the value of  $k_{ij}$  to be estimated. Therefore, a default value of 0 was used. The calculations indicate that SF<sub>6</sub> is more soluble in DHN than CO<sub>2</sub> by a factor of about 2. If this estimate of SF<sub>6</sub> solubility is directionally correct, it suggests that dissolved SF<sub>6</sub> is more effective in reducing the solution viscosity than dissolved CO<sub>2</sub>, on a molecule-for-molecule basis. However, this interpretation should be viewed with great caution until it is supported by experimental data.

### CONCLUSIONS

The viscosity of 1–15 wt % PS in DHN was measured for two different molecular weights over a range of temperature up to 150°C. The low-temperature data agreed reasonably well with values previously reported for PS in DHN at 25°C. The concentration range investigated was in the semidilute (coil overlap) region, between the dilute and fully concentrated regimes. The solution viscosity increased with the concentration, as described by the Martin equation, and increased with the molecular weight, as described by  $\eta_r = f(c\sqrt{M_n})$ . In the absence of CO<sub>2</sub>, the relative viscosity increased with the polymer concentration approximately exponentially. The application of CO<sub>2</sub> to the PS/DHN solutions caused a significant decrease in the viscosity. The largest viscosity reductions occurred for the highest polymer concentrations, the lowest temperatures, and the highest  $M_n$  polymer. The uniqueness of CO<sub>2</sub> for viscosity reduction was evaluated by a comparison of the viscosity reduction with CO<sub>2</sub> to the viscosity reduction with SF<sub>6</sub>. At the same gas pressure, the reduction in viscosity with SF<sub>6</sub> was comparable to that with CO<sub>2</sub>.

These studies suggest that CO<sub>2</sub> can be a valuable tool for controlling the viscosity of polymer solutions

and improving the transport properties of polymers in solutions.

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