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Notes

Viscosity Reduction of Polystyrene Solutions in Toluene with Supercritical Carbon Dioxide

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Introduction

Viscosity of polymer solutions at high pressure is of great interest in processing of polymers using near-critical and supercritical fluids.[1,2] Viscosity plays an important role in the transport and kinetic aspects of high-pressure polymerization and in the post-polymerization processing of polymers for production of microstructured materials that cover a range from particles to fibers or foams.[2,3] A specific area of recent activity is the modification of viscosity of polymer melts with addition of supercritical fluids as processing aids.[4,5]

Several systematic studies have already been reported on the high-pressure viscosity of polymer solutions such as polystyrene in *n*-alkanes[6,7] (*n*-butane, *n*-pentane, and *n*-hexane), methylcyclohexane,[8] and toluene,[9] polyethylene in *n*-pentane,[10] and poly(dimethylsiloxane) in carbon dioxide.[11] More recently, we have been investigating the viscosity of "polymer + solvent + carbon dioxide" ternary mixtures.[9] In this context, we evaluated the pressure, temperature, density, and concentration dependence of viscosity of a relatively low molecular weight ($M_w = 50\,000$) polystyrene sample in toluene + carbon dioxide mixtures. It has been demonstrated that, at the same overall mass density of the solutions, the solutions that have the higher carbon dioxide content show lower viscosities. The lower viscosity at the same solution density (which at a given temperature may correspond to a different pressure condition depending upon composition) becomes more apparent for solutions at higher polymer concentrations (up to 7% that was evaluated) and at lower temperatures that would correspond to higher initial, carbon dioxide-free base viscosity for the solutions.

The behavior of ternary solutions with carbon dioxide as a component is of relevance to pressure-tunable solvent−antisolvent processing of polymers that use supercritical carbon dioxide as the antisolvent component. In this paper, we now report on the change in the viscosity in solutions of a high molecular weight ($M_w = 700\,000$) polystyrene sample in toluene at high pressure upon addition of supercritical CO_2. This is a focused study on polystyrene solutions with a polymer concentration of 1.5 wt % in toluene forming the base solution. Viscosity was determined upon addition of various levels of carbon dioxide up to 14.0 wt % (i.e., 14.0% CO_2 + 86.0% base solution) into the base polymer solution. The measurements were conducted using a falling-cylinder type viscometer at 320 K in the pressure range 10−40 MPa. The results show an exponential decrease in viscosity of the base solution that could be correlated with a relatively simple relationship. A phase diagram for the polystyrene + toluene + CO_2 ternary system is also presented to ensure that all viscosity measurements have been conducted under homogeneous solution conditions.

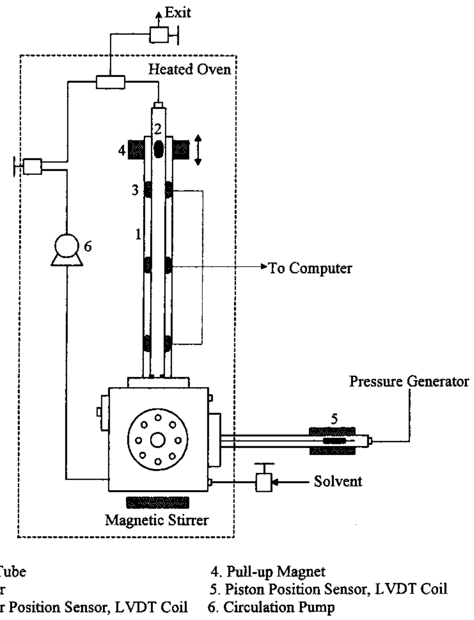

Figure 1. Schematic diagram of the experimental apparatus for density and viscosity measurements.

Experimental Section

Materials. The polystyrene sample of weight-average molecular weight of 700 000 with a polydispersity of $M_w/M_n \leq 1.26$ was purchased from Pressure Chemical Co.

Viscometer. Figure 1 is a schematic illustration of the falling-cylinder type viscometer used in this study. Details have been described in our earlier publications.[6−11] Briefly, the system consists of a high-pressure view cell equipped with a movable piston, a fall tube (1), and a sinker (2). Location of the sinker during fall is detected by the three LVDT (linear variable differential transformer) coils (3) positioned along the fall tube which permit determination of the fall time. A pull-up magnet (4) is used to reposition the sinker at the top of the fall tube. An additional LVDT device (5) detects the position of the movable piston that permits the determination of internal volume of the cell, from which densities are determined. A high-pressure circulation pump (6) is used to circulate the cell content to obtain homogeneous conditions.

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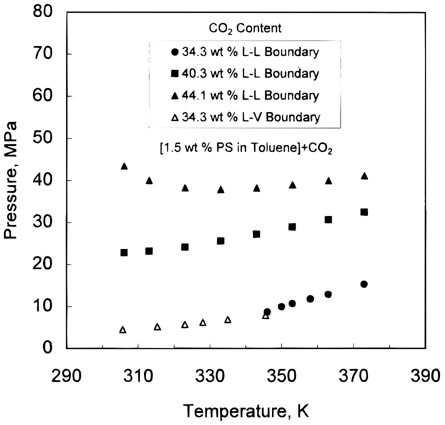

Figure 2. Phase separation boundary of [1.5 wt % polystyrene solution in toluene] + CO_2 mixtures at CO_2 concentrations of 34.3, 40.3, and 44.1 wt % in the mixtures.

Viscosity Measurements. The polystyrene solution of 1.5 wt % in toluene was prepared inside the viscometer as a base solution. Density and viscosity of the CO_2-free polymer solution were measured at 320 K in the pressure range 10−40 MPa. After the viscosity measurements on the base solutions were completed, a known amount of CO_2 was injected into the system, generating a ternary mixture of polystyrene + toluene + CO_2. Viscosity measurements were conducted for the ternary mixtures at various CO_2 concentrations up to 14.0 wt %.

Phase Boundary Measurements. Phase separation boundaries for the ternary mixtures of polystyrene + toluene + CO_2 were determined independently by using a dedicated variable-volume view cell apparatus.[12] The phase boundary for each mixture was determined by visual observation of the cloud-point pressure at constant composition and temperature. The cloud-point data were obtained after a known amount of CO_2 (up to 44.1 wt %) was added to an initial polymer solution containing 1.5 wt % polystyrene.

Results and Discussion

Phase separation boundaries for the polystyrene + toluene + CO_2 ternary system are displayed in Figure 2. In this figure, the regions above each curve are the one-phase regions. At lower carbon dioxide addition levels, the liquid−liquid phase boundary is that of LCST (lower critical solution temperature) type with the two-phase region being entered upon an increase in temperature at a given pressure. As shown in the figure, with increasing CO_2 concentration the liquid−liquid phase boundary shifts to higher pressures accompanied also by a shift toward UCST (upper critical solution temperature)-type behavior in the lower temperature range over which the system now enters the one-phase region upon an increase in temperature. Such crossover from LCST- to UCST-type behavior in ternary polymer + solvent + carbon dioxide systems that occurs with increased carbon dioxide content is known for other polymer solutions such as polyethylene + pentane + carbon dioxide.[13,14] At a CO_2 concentration of 34.3 wt %, the LCEP (lower critical end point), where the LCST branch touches vapor−liquid-phase boundary, was observed at 345.5 K and 7.9 MPa. Previous researchers have shown that for the polystyrene + toluene + CO_2 system the LCEP temperature moves to a higher temperature as CO_2 concentration in the mixture is lowered.[15] Therefore, the ternary mixtures investigated in the present viscosity measurements, for which the maximum CO_2 concentration is 14.0 wt %, exists as homogeneous one-phase solutions at the temperature (320 K) and the pressure range (10−40 MPa) investigated.

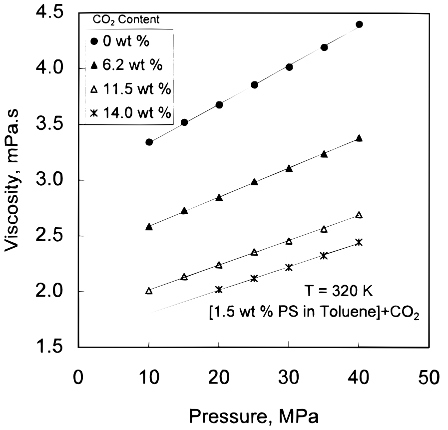

Figure 3. Viscosity variation of [1.5 wt % polystyrene solution in toluene] + CO_2 mixtures as a function of pressure at 320 K.

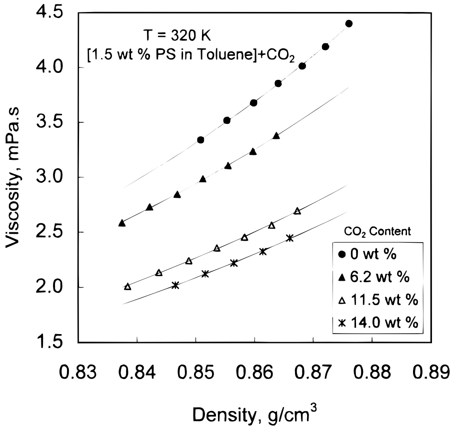

Figure 4. Viscosity variation of [1.5 wt % polystyrene solution in toluene] + CO_2 mixtures as a function of mixture density at 320 K.

Figure 3 shows the viscosity variation of the base solution of 1.5 wt % polystyrene in toluene at various levels of CO_2. The data are presented as a function of pressure at 320 K. It should be noted that compared to polymer melts, or concentrated solutions, the viscosities for the present system are very low (being in the mPa s, instead of Pa s range) at these concentrations. However, as shown in the figure, significant viscosity reduction still occurs upon addition of CO_2 at constant pressure. Viscosity of these ternary mixtures exhibits a linear variation with pressure in the pressure range investigated. Pressure sensitivity of viscosity ($\partial\mu/\partial P$) appears to decrease with increasing CO_2 content in the mixtures, suggesting a reduction in flow activation volume.

Figure 4 demonstrates the viscosity reduction in the density domain of the ternary mixtures at 320 K in the pressure range 10−40 MPa. Density of the mixtures ranged from 0.84 to 0.88 g/cm^3 at these experimental conditions. This figure permits comparison of the viscosity of solutions at the different CO_2 concentrations at a given density (or apparent free volume). As shown, the polystyrene solutions of the same overall mixture density displayed different viscosity at different CO_2 concentration in the mixture. As in the case with pressure dependence, at this constant temperature, sensitivity of the viscosity on mixture density decreased as CO_2

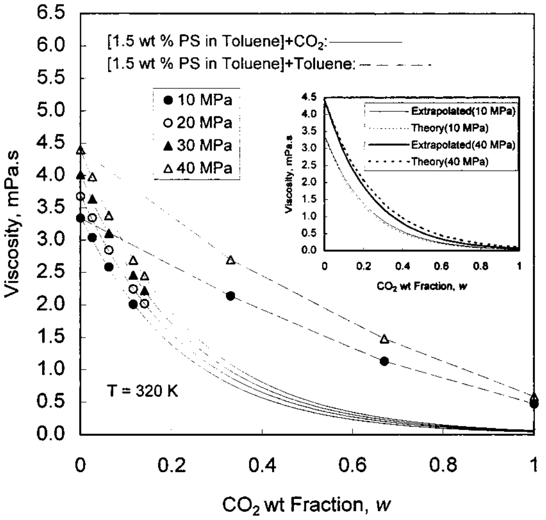

Figure 5. Viscosity reduction of 1.5 wt % polystyrene solutions in toluene upon addition of CO$_2$ at various pressures and at 320 K. Solid curves represent the regression of data from CO$_2$ addition. Dashed curves stand for viscosity variation of the base solution upon addition of the same mass of toluene instead of CO$_2$. The inset compares the viscosity predicted by forcing $A = \mu_1$ and $B = \ln(\mu_1/\mu_2)$ in eq 1 (dotted curves) with the extrapolation based on the best-fit curves to the experimental data (solid curves) at 10 and 40 MPa.

concentration increased in the mixtures. The average rate of change of viscosity with the mixture density, expressed in units of (mPa s)/(g cm^{-3}), that were calculated from the data are 41.3, 29.8, 23.2, and 21.7 for the 0, 6.2, 11.5, and 14 wt % carbon dioxide containing solutions, respectively.

Figure 5 illustrates the viscosity reduction of the solutions as a function of the CO$_2$ concentration (expressed as weight fraction, *w*) in the ternary mixtures at various pressures. Experimental data points correspond to CO$_2$ weight fraction up to $w = 0.14$ in the mixture. The data were regressed using an exponential function of the form

$$\mu = A \exp(-Bw) \qquad (1)$$

where μ is viscosity of the mixture, *w* is CO$_2$ weight fraction, and *A* and *B* are constants. [Even though polymer solution viscosities are more commonly correlated with exponential expressions involving parameters that depend on polymer volume fractions,[16] we have adopted this relationship based on directly measured weight fractions for practical convenience.] The resulting curves were extrapolated to pure CO$_2$ ($w = 1.0$). The viscosity values at $w = 1.0$ that are predicted from the best-fit curves were 0.039, 0.048, 0.055, and 0.063 mPa s at 10, 20, 30, and 40 MPa, respectively. These are found to be approaching the actual viscosity of pure CO$_2$ at the respective pressures. The viscosity values of pure CO$_2$ at 320 K are 0.032, 0.071, 0.087, and 0.101 mPa s at 10, 20, 30, and 40 MPa, respectively.[17] This observation suggests that a simple exponential function (eq 1) can be used to correlate the viscosity reduction of polymer solutions upon addition of CO$_2$. It is important to note that this extrapolation implicitly assumes that at the prevailing pressures the mixture is fully homogeneous. Any estimation from such a relationship would not be valid if two-phase regions are entered (due to high carbon dioxide level or pressure not being high enough), and therefore the validity of the solid curves beyond the experimental data points should not be viewed as experimentally verified. Nonetheless, eq 1 must give the viscosity of CO$_2$-free base solution (μ_1) when $w = 0$ and the viscosity of pure CO$_2$ (μ_2) at $w = 1.0$, which then would require that $A = \mu_1$ and $B = \ln(\mu_1/\mu_2)$. For this system $\mu_1 = 3.341$, 3.678, 4.014, and 4.401 mPa s at 10, 20, 30, and 40 MPa, respectively. The inset in Figure 5 compares the curves when eq 1 is forced to satisfy the limiting conditions for data at 10 and 40 MPa. There is very little difference between the predicted and the extrapolated values of viscosity. Therefore, the viscosity of the ternary mixtures at any CO$_2$ concentration can be estimated from the viscosity data of base polymer solution and pure CO$_2$ at a given temperature and pressure as long as the mixture is in the one-phase region. Of course, as the CO$_2$ concentration is increased, the polymer solution may eventually undergo phase separation into polymer-rich and solvent-rich phases at certain elevated CO$_2$ concentration. For example, at 40 MPa, according to Figure 2, phase separation will occur approximately at $w = 0.45$ at 320 K.

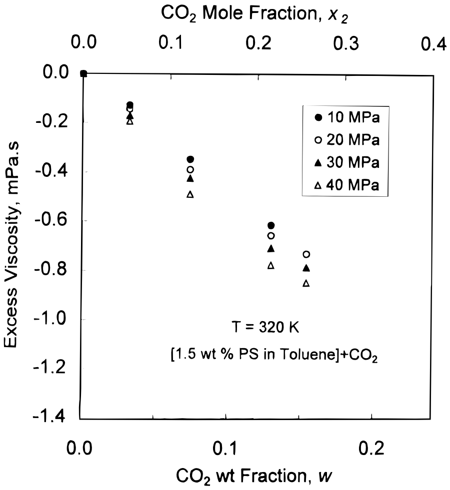

Figure 6. Viscosity deviation (excess viscosity) for the system [1.5 wt % polystyrene solution in toluene] + CO$_2$ mixtures at various pressures and at 320 K.

Clearly, the viscosity reduction shown in Figures 3−5 is in part due to the decrease in the overall polymer concentration in the solution upon addition of carbon dioxide. To give a measure of the decrease that would have occurred due to reduction in polymer concentration in Figure 5, we have included the viscosity of the solution if, instead of CO$_2$, more toluene had been added to the system. These are shown by the dotted curves which indicate a more gradual decrease in viscosity as a result of mere lowering of the polymer concentration, compared to the exponential decrease in the presence of carbon dioxide. Therefore, it is clear that the presence of CO$_2$ contributes more to the viscosity reduction.

The viscosity deviation of the mixture from a linear combination of each component's viscosity can be described by the excess viscosity, μ^E, expressed as

$$\mu^E = \mu - (x_1\mu_1 + x_2\mu_2) \qquad (2)$$

where x_1 and x_2 are mole fractions of the base polymer solution and CO$_2$, respectively. In this expression, the ternary mixture was considered as pseudobinary mixture of base polymer solution + CO$_2$. Figure 6 shows the excess viscosity of the base polystyrene solutions in toluene as a function of CO_2 mole fraction or weight fraction at 20, 30, and 40 MPa. [Even though expressing the excess quantities in mole fraction is the common practice,[18] we find representations in weight fractions to be of practical value.] It was found that the present polymer solution exhibits negative excess viscosity behavior upon addition of CO_2, and the negativity appeared to increase with pressure.

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