고분자 용액의 고압 밀도 및 점도 측정과 첨가된 CO_2의 영향

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High-Pressure Density and Viscosity of Polymer Solutions and the Effect of Carbon Dioxide

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Introduction

Information on the volumetric and transport properties of polymer solutions is crucial for the design and operation of polymer processes. Among the properties of polymer solutions, high-pressure density and viscosity data are especially important in a variety of applications such as high-pressure synthesis, molten polymer processing and lubrication with polymer additives. The solution viscosity is a valuable parameter that can be used in molecular weight determinations. It gives a measure of the molecular size and chain coil dimensions that depends on polymer-solvent interactions, chain overlap and entanglements in solutions.

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 anti-solvents 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. [1] As anti-solvents, high-pressure gases are used in diverse applications that rely on the alteration of phase boundary of polymer-organic solvent mixtures [2] as in the solvent-induced particle formation processes. [3] Studies have also been reported on the phase boundary shift in polymer-organic solvent mixtures in the presence of high-pressure gases that lead to the expansion of the liquid-liquid region that facilitates polymer fractionation. These systems are composed of ternary mixtures that are made up of organic solvent, polymer and a high-pressure gas such as carbon dioxide.

In this paper, we report the density and viscosity data for solutions of nearly monodisperse polystyrene in methylcyclohexane and toluene. Also, the viscosity of dilute solutions in the mixtures of toluene and CO_2 has been measured. The solution densities and viscosities were determined using a falling-ball type viscometer as a function of pressure, temperature, and the concentration of 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.

Experimental Methods

The polystyrene samples of weight average molecular weight of $M_w = 50{,}000$, $M_w/M_n \leq 1.06$ and $M_w = 700{,}000$, $M_w/M_n \leq 1.26$) were purchased from Pressure Chemical Co. Methylcyclohexane and toluene with purities of 99.8 % were obtained from Aldrich Chemical Co. Carbon dioxide with a minimum purity of 99.8 % was obtained from Airco Co.

Figure 1 shows the schematic diagram of the falling-ball type high-pressure viscometer. This viscometer permits the simultaneous measurement of density and viscosity of polymer solutions up to 470 K and 70 MPa. The apparatus is equipped with a view window that permits 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. The movement of the sinker in the fall-tube is followed by the three LVDT coils to measure the fall time and hence to determine the viscosity of the solution. A pull-up magnet is used to bring the sinker to the top position of the fall-tube. A high-pressure circulation pump is used to circulate the internal solution to maintain the temperature and concentration homogeneous. Details of the design and operating procedure can be found in our previous articles. [4,5]

Density and viscosity measurements were carried out with the solutions of polystyrene in pure solvents as well as in solvent + CO_2 mixtures. First, a measured amount of the polystyrene sample is charged to the cell through the solute loading port. The system is then purged several times with gaseous CO_2 to remove air that may have been trapped inside the cell. A known amount of solvent 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_2 from the cell. This procedure generates a target composition of the polystyrene solution in pure solvent. 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. Now a known mass of CO_2 is injected to the system in addition to the polymer solution, resulting in a ternary mixture of polystyrene + solvent + CO_2. 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_2 can readily be determined.

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. Viscosity is determined by measuring the fall time of the sinker passing through the three LVDT coils.

Results and Discussion

The density variation of a polystyrene solution in methylcyclohexane is shown in Figure 2. As expected, the density increases with pressure and decreases with temperature. Density of the pure solvent and of all the polymer solutions exhibit linear variation with pressure at constant temperatures under the concentration and molecular weight ranges investigated. The rate of increase in density as a function of pressure, i.e. the solution compressibility $\Delta\rho/\Delta P$, ranged from 0.0009 to 0.0013 g/cm^3 per 1 MPa increment for all polymer solutions.

The viscosity of the polystyrene solutions in methylcyclohexane is given in Figure 3. The variation of viscosity with pressure shows the linear trend at all temperatures, concentrations and molecular weights investigated. As expected, the viscosity significantly influenced by polymer concentration and molecular weight. For 50,000 molecular weight polystyrene, the viscosity moderately increased with concentration in the low concentration range (3-9.5 wt %). However, the change in concentration from 9.5 to 14 wt % leads to a very large viscosity increase. The large increase in viscosity may be the result of chain entanglements. For 700,000 molecular weight polystyrene, the viscosity proportionally increased with concentration in the range from 1 to 5 wt %. Overall, viscosity of the 3 wt % solution of 700,000 molecular weight sample was about 2.5 times greater than that of the 50,000 molecular weight sample.

The pressure dependency of viscosity at a constant temperature can be described in terms of flow activation volume through the following equation.

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

where η is viscosity, A a constant, $V^{\#}$ the flow activation volume, P the pressure, R the gas constant and T is the temperature. The activation volumes of the polystyrene solutions were calculated from the slop of $\ln\eta$ *vs* P plots at each temperature and concentration. The evaluated activation volume ranged from 29 to 55 cm^3/mol. The activation volume increased with temperature at all concentrations and molecular weights, showing that at a higher temperature, the viscosity becomes more pressure dependent for the present polymer solutions. Larger activation volume was obtained for the higher molecular weight sample, indicating an increasing effective size for the flow unit. The variation of polymer concentration, however, did not generate a clear trend in the values of activation volume under the concentration range investigated.

The temperature dependency of viscosity for polymer solutions is found to follow the simple exponential Arrhenius type equation.

$$\eta = A\, exp(E/RT) \qquad (2)$$

where A is a constant and E is the flow activation energy. The activation energies of the polystyrene solutions were evaluated from the slop of $\ln\eta$ *vs* $1/T$ plots at each pressure and concentration. The calculated activation energy ranged from 7 to 10 kJ/mol. Generally, the activation energy decreased with pressure at all concentrations and molecular weights, showing that at a higher pressure, the viscosity becomes less temperature dependent. The activation energy was found to be essentially not affected by concentration and molecular weight in the range investigated in the present study.

Figure 4 shows the variation of viscosity as a function of density of the polystyrene solutions. As expected, the density dependence of viscosity increased with polymer concentration. In Figure 4, viscosity data at different pressures and temperatures collapse to a single curve, confirming that the density can be an effective scaling factor for the viscosity. Therefore, viscosity can be represented as a mathematical function with density as an independent variable. In this study, a Doolittle type equation [6] with 3 parameters has been adopted to correlate the present data, i.e.

$$\eta = A\,exp\{(B/(1-V_o\,\rho))\} \tag{3}$$

where η is viscosity of the mixture, A and B are constants, ρ is the density and V_o is the closed-packed volume. The estimated closed-packed volumes were in the range of 0.67-0.68 cm^3/g for 50,000 molecular weight solutions and 0.66-0.72 cm^3/g for 700,000 molecular weight solutions. Even though can not be generalized, there is indication that the closed-packed volumes for the solutions increase with polymer concentration and with molecular weight.

Figure 5 shows the viscosity variation for base solutions of 7 wt % polystyrene in toluene upon addition of various levels of CO_2. The viscosity of the polymer solutions in pure toluene and in toluene + CO_2 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_2 concentration increased. At the same CO_2 addition level, the reduction in viscosity was observed to be greater in solutions of higher polymer concentration.

Figure 6 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,

$$\eta = A\,exp(-Bw) \tag{4}$$

where w is CO_2 weight fraction and A and B are constants. The resulting curves were extrapolated to pure CO_2 ($w = 1.0$), and the results were found to be approaching the actual viscosity of pure CO_2 at the respective pressures. This observation suggests that a simple exponential function can be used to correlate the viscosity reduction of polymer solutions upon addition of CO_2. The inset in Figure 6 compares the curves when Eq. (4) is forced to satisfy the limiting conditions for data at 10 and 40 MPa. There is very little difference between the predicted and the experimental 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.

References

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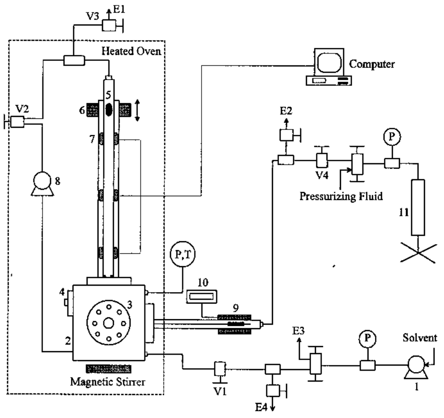

Figure 1. Experimental apparatus. High-pressure falling-ball type viscometer.

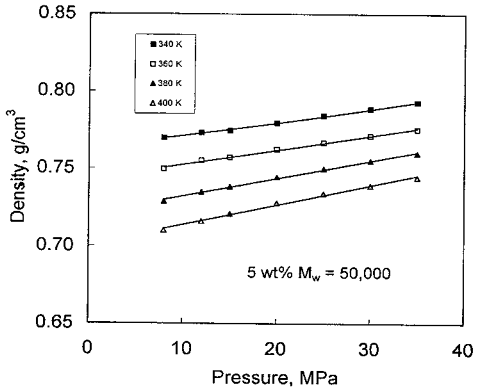

Figure 2. Density of polystyrene solution as a function of pressure.

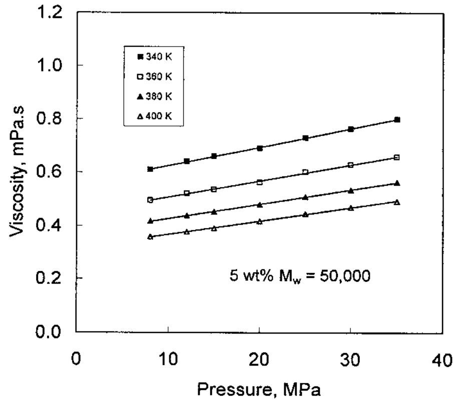

Figure 3. Viscosity of polystyrene solution as a function of pressure.

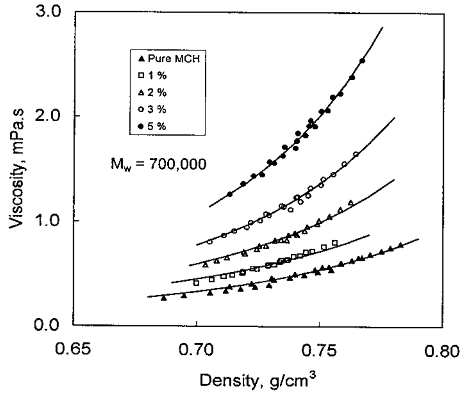

Figure 4. Viscosity of polystyrene solution as a function of density.

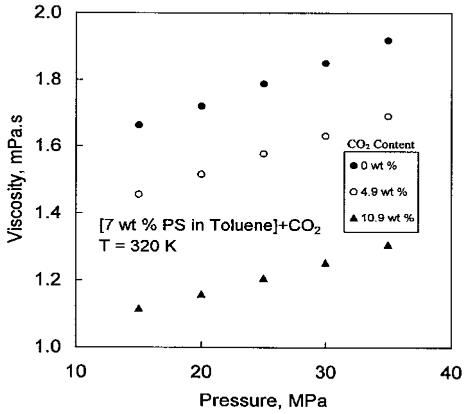

Figure 5. Viscosity of polystyrene solution in the presence of CO_2.

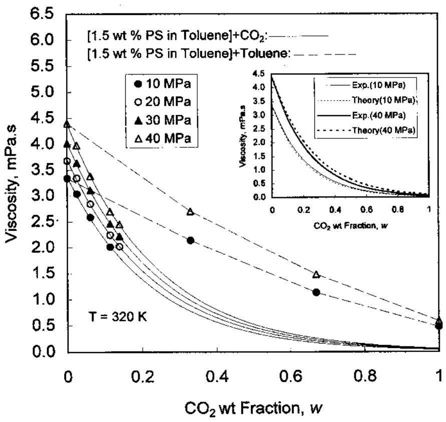

Figure 6. Viscosity reduction of polystyrene solution with the addition of CO_2.