CHAPTER 3

LITERATURE REVIEW ON POLYMER SOLUTION VISCOSITY AT HIGH PRESSURES

Viscosity is a key fundamental property which plays an important role in fluid transport, mixing, heat transfer or mass transfer operations. Polymer solution viscosities at high pressures are also of importance in reactive systems such as polymerizations. The viscosity database for polymer solutions at high pressures is very limited. This has in part been due to the limitations of instruments suitable for viscosity measurements at high pressures. In this chapter, we provide a short review of viscosity measurement methods and polymer solution viscosity at high pressures.

3.1 High-pressure viscometers

A range of techniques have been explored for high pressure viscosity measurements. The viscometers used broadly categorized as capillary, rotational, falling body, magnetic, acoustic, and slit die rheometers. They are summarized in Table 3.1.

3.1.1 Capillary tube viscometer

The capillary viscometers are the most widely used viscometer. (Wisniewshi et. al., 2003, 2005; Barrufet and Setiadarma, 2003; Bhide et. al., 2003).

It is based on the Hagen-Poiseuille law given by

$$\Delta P = 8L\mu Q / \pi R^4 \qquad \text{(Eq.3.1)}$$

where ΔP is the pressure difference across the capillary tube, L and R are the length and radius of the capillary tube, Q is the volumetric flow rate, and μ is the viscosity of the fluid flowing through the capillary tube. The use of the Hagen-Poiseuille law requires that the fluid is incompressible and Newtonian, the flow is steady-state and laminar, and the slip at the wall can be neglected. Care must be excercized in using capillary viscometer at high pressures to correct for compressibilities due to the pressure gradient along the capillary (Sun and Storvick, 1979).The pressure difference between the two ends of the capillary tube and volumetric flow rate through the tube are needed to find the viscosity. A differential pressure sensor is used to measure the pressure difference. A range of methods are used to determine the volumetric flow rate. A displacement fluid such as mercury, mineral oil can be used to determine flow rate by measuring the volume change of the displacement fluid with time (Boned et. al., 2003; Sun and Storvick, 1979; Rutherford, 1998). Optical windows have been used to read the liquid level change in the two reservoirs with time to determine the flow rate (Bhide et. al., 2003; Ripple, 1992). A constant flow pump has been reported to transfer liquid through the capillary tube with known flow rate (Gozalpour, 2005).

3.1.2 Falling-body/ rolling-body viscometer

According to Stokes' falling sphere principle, the viscosity η of a Newtonian fluid can be expressed as

$$\eta = (2/9)(\rho_s - \rho)gR^2 / V_t \qquad \text{(Eq.3.2)}$$

where ρ_s and R are the density and radius of the sphere, g is the gravitational acceleration, V_t is the terminal velocity of the sphere (Deen, 1998). For a given sphere with known density and radius, once the terminal velocity is determined, the viscosity of the fluid can be readily calculated. For rolling-ball viscometers, similar to the falling-ball viscometers, the speed of the rolling sphere down in a cylindrical tube inclined at a fixed angle to the horizontal is used to determine the velocity. For the falling-body viscometers with a cylindrical sinker, the working equation for the viscosity of Newtonian fluid is given by,

$$\eta = \frac{t(\rho_s - \rho)(r_1^2 g)[(r_2^2 + r_1^2)\ln(r_2 / r_1) - (r_2^2 - r_1^2)]}{2L(r_2^2 + r_1^2)} \qquad \text{(Eq.3.3)}$$

where η and ρ are viscosity and density of the fluid, ρ_s is the density of the cylindrical sinker, t is the falling time, L is the vertical fall distance, r_1 and r_2 are radius of the cylinder and inner radius of the falling tube, respectively (Dindar, 2001).

These viscometers are designed to insure “self-centering” for the falling body. The ratio of radius of the falling cylinder to that of the tube is maintained to be larger than 0.93 (Sen and Kiran, 1990). Equation 3.2 is usually modified to a practical working equation for falling-body viscometers,

$$\eta = K(\rho_s - \rho)/V_t \qquad \text{(Eq.3.4)}$$

where η and ρ are once again the viscosity and density of the fluid, ρ_s is the density the sinker, V_t is the terminal velocity of the sinker, and K is the calibration constant. To find the viscosity η of the fluid, fluid density and terminal velocity of the sinker are needed. Terminal velocities are determined from visual (or optical) or electric measurements of the sinker position with time (Nakamura and Kurosaki, 2005; Dindar and Kiran, 2002a,b; Terasaki et. al., 2001).

Suitable for low viscosity measurement, the falling/rolling body viscometer is a reliable method to provide high-precision viscosity data. However, it is of limited viscosities for system with very high viscosity due to extremely long fall times. This is the viscometer type that is used in the present study and the system specifications and operational details are presented in Chapter 4.

3.1.3 Rotational viscometer

Rotational viscometers are based on the analysis of the steady flow in the annular gap between long, coaxial cylinders, one or both of which is rotated at a constant angular velocity, known as Couette viscometers (Deen, 1998). For the case that the inner cylinder is rotated and the outer one is fixed, the viscosity η can be related to the torque G required to turn the outer cylinder as follow,

$$\eta = \frac{G}{2\pi L w}\left(\frac{1}{R_1^{2} - R_2^{2}}\right) \qquad \text{(Eq.3.5)}$$

where R_1 is the outer radius of the inner cylinder, R_2 is the inner radius of the outer cylinder, L is the wetted length of the cylinders, w is the angular velocity of the inner cylinder. According to the geometry, there are four types, namely, coaxial cylinder, rotating disk (parallel-plate), cone-and-plate, and rotating spindle viscometers. However, for applications at high pressures, the first three have been used more frequently (Khandare et. al., 2000a,b; Ahemed and Rammaswamy, 2003,2004; Vaisburd and Brandon, 1997; Peticolas and

Watkins, 1957; Wolf and Jend, 1979; Bair, 2001a,b; Kinzl et. al., 2003; Flich et. al., 2005; Horst et. al., 1998).

Rotational viscometers are suitable for high viscosity measurements, and allow adjustments of the shear rate. However, there are difficulties in loading and controlling the pressure in high-pressure applications. They are not suitable for low viscosity measurements since the torques required by the low viscous medium are small for sensitive measurements to be conducted.

3.1.4 Magnetoviscometer

Similar to falling/rolling body viscometer, according to Stokes' falling sphere principle (Deen, 1998),

$$F = 3\pi d \eta v_{\infty} \qquad \text{(Eq.3.6)}$$

where F is the force on the sphere, d is the diameter of the sphere, v_{∞} is the terminal velocity of the fluid, η is the viscosity of the fluid. The force here can be gravity (weight) for falling/rolling-body viscometers; it can also be a magnetic force. In the magnetoviscometer, the magnetic force is used instead of the gravity (Mattischek and Sobczak, 1994). The magnetic force is expressed as

$$F_m = mX_m H \frac{dH}{dz} \qquad \text{(Eq.3.7)}$$

where F_m is the magnetic force on the sphere with mass m and susceptibility X_m, H is the magnetic field strength, $\frac{dH}{dz}$ is the field gradient, and z is the direction of the forced sphere motion.

With application of the magnetic field the shear rate can be adjusted. The magnetoviscometer has been reported for both low and high viscosity measurements (Mattischek and Sobczak, 1994). Commonly, this technique is limited to low-viscosity fluids.

3.1.5 Magnetically levitated sphere rheometer

A magnetically levitated sphere rheometer for polymer solutions and melt was developed recently (Royer et. al., 2002). A sphere was levitated at a fixed position in the test fluid inside the high-pressure housing by a magnetic field. By moving the cylindrical tube vertically, a shear flow was generated. The sphere would move with the shear slow if no forced was exerted on the sphere. The magnetic force needed to maintain the position of the sphere is then related to the viscosity of the test fluid. The technique requires extensive calibrations for accurate viscosity measurements.

3.1.6 Extrusion slit die rheometer

High-pressure extrusion die slit viscometer is a modified capillary tube viscometer suitable for high viscosity measurements such as polymer melts (Royer et. al., 2000, 2001; Lan and Tseng, 2002). The viscosity of a polymer melt is calculated from the following equations (Royer et. al., 2000, 2001),

$$\text{Sheer stress } \tau_w = \left(\frac{-\Delta P}{L}\right)\frac{H}{2} \qquad \text{(Eq.3.8)}$$

$$\text{Apparent shear rate } \dot{\gamma} = \left(\frac{6Q}{wH^2}\right) \qquad \text{(Eq.3.9)}$$

Apparent viscosity $\eta_{app} = \dfrac{\tau_w}{\dot{\gamma}_{app}}$ (Eq.3.10)

where L is the length of the slit, w the slit width, H the slit height, ΔP the pressure drop, and Q the volumetric flow rate.

The viscometer is suitable for high-viscosity measurement with control on shear rate and can access non-Newtonian behaviors. However, it is not suitable for systems that show low viscosity.

3.1.7 Sliding plate viscometer

In these viscometers, the medium to be tested is charged in between two parallel sliding plates. After shear rate and shear stress are measured, the viscosity can be readily evaluated according to the general defining equation of viscosity (Koran and Dealy, 1999a, b).

$$\tau = \eta \dot{\gamma} \qquad \text{(Eq.3.11)}$$

The principle of operations of sliding plate viscometer is simple, and it is suitable for high-viscosity measurement such as polymer melts. However, they are not suitable for low-viscosity measurements.

3.2 Polymer solution viscosity at high pressures

Using the methods introduced in Section 3.1, various polymer solution viscosities have been experimentally determined over wide range of temperatures and pressures. These are summarized in Table 3.2 for solutions at low or moderate polymer concentrations, and in

Table 3.3 for solutions with moderate and high polymer concentrations or melts containing supercritical fluids.

Viscosity of the polymer solutions with a major component of solvent is of great importance in polymer film casting, polymer fiber preparation, polymer particle formation (RESS, GAS, SAS, SEDS process), and polymerizations. Dilute solution viscosity data is also important to explore the interactions between the polymer and the solvent by finding out if the solvent is "good" or "poor" solvent, which is inferred from relationships such as the Mark-Houwink equation

$$[\eta] = KM^{\alpha} \qquad \text{(E.q.3.12)}$$

where K and α are two constants, M is the polymer molecular weight. The exponent α ranges from 0.5 to 2.0. If this exponent is close to or larger than 0.75, the solvent is a "good" one, in which the polymer chain is fairly extended. If it is close to 0.5, the solvent is a "poor" one, in which the polymer chain displays a tight configuration.

The early studies in the polymer solution viscosity at high pressures are focused on the viscosity measurement as well as probing the interaction between polymer and the high-pressure solvent. In 1979, Kubota and coworkers (Kubota and Ogino, 1979) measured the pressure dependence of the intrinsic viscosity of poly (dimethylsiloxane) – cyclohexyl bromide solutions over the pressure range of 1 – 40 MPa and the temperature range of 25 – 45 °C using a rolling-body type viscometer. The intrinsic viscosity and the chain dimensions were observed to increase with an increase of pressure, suggesting that the solvent becomes a "better" solvent for the polymer with increasing pressure. Wolf and coworkers (Wolf et. al.,

1979) measured the pressure and temperature dependence of the viscosity for the system *trans*-decahydronaphthalene / polystyrene over a pressure range of 1 - 1000 bar at shear rates in the range 20 – 320 s^{-1} using a rotational viscometer. They showed that viscosity measurements can detect phase separation in this system. This is schematically illustrated in Figure 3.1.

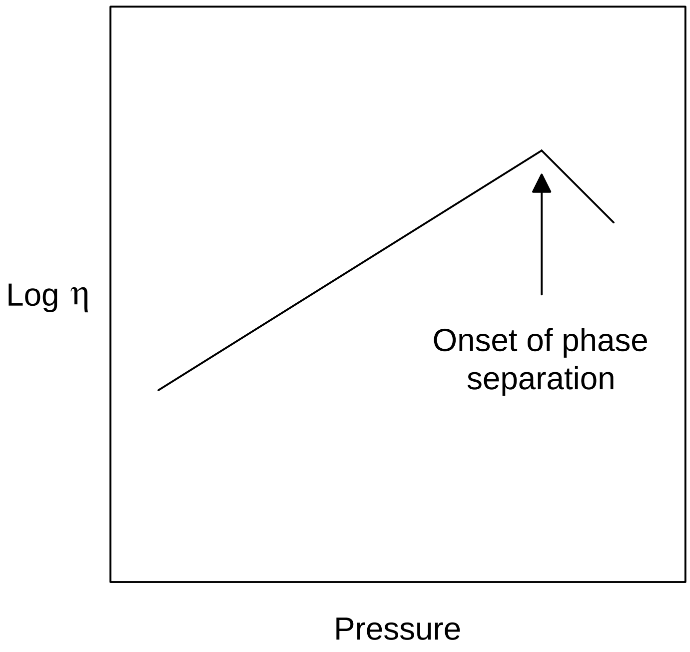


Figure 3.1 Schematic diagram of phase separation during viscosity measurement. Generally, the viscosity increases with pressure. When the phase separation takes place, the viscosity shows decrease with pressure, which can be used to detect the phase separation in the system.

In 1992, Cook and coworkers measured the viscosity of polystyrene, Zinc sulfonated polystyrene, and poly (styrene-4-vinylpyridine) in THF at pressures up to 20 kbar using the falling body viscometer (Cook et. al., 1992a). They showed that in a associated system such as solutions of ZnSPS/PSVP in THF, viscosities may show abnormalities compared to common polymer solutions. They reported instead of a decrease in intrinsic viscosity with pressure, and an unusual, abrupt, reversible rise in viscosity at pressure of 2 kbar. They also reported on the high-pressure viscosities of dilute polymer solutions of polystyrene in THF or chloroform, polyisobutylene in THF using a falling-body viscometer at pressures up to 20 kbar with a diamond-anvil cell as high-pressure vessel (Cook et. al., 1992b). The viscosities of the these polymer solutions were found to increase faster than the pure solvents with increasing pressure. Compared with the data of the same system at ambient pressure, they found the specific viscosity and intrinsic viscosity was independent of pressure within the pressure range investigated.

Kiran and coworkers have been collecting systematic viscosity data for polymer solutions at high pressures since 1993 using a falling-cylinder type high pressure viscometer. The solution viscosity and density were experimentally determined for PS in n-butane (Kiran and Sen, 1993), PE in n-pentane (Kiran and Gokmenoglu, 1995), PDMS in CO_2 (Xiong and Kiran, 1995; Dindar and Kiran, 2002a), PS in n-hexane (Xiong and Kiran, 1997), PS in methylcyclohexane (Yeo and Kiran, 1999), PS in toluene + CO_2 (Yeo and Kiran, 1999a,b) over a wide ranges of temperatures and pressures. Significant viscosity reductions were reported upon addition of modest levels of CO_2 to solutions of PS in toluene (Yeo and Kiran, 1999a, b). The reduction in viscosity reduction with CO_2 is important in processing of polymers from polymer solutions, or melts.

A different area of application for viscosity at high pressures is enhanced oil recovery, where there is intent in using carbon dioxide to displace oil. However, at reservoir conditions, viscosity of CO_2 (0.03 – 0.10 cP) is much lower than that of reservoir oil (0.1 – 50 cP) which hinders the use. There has been an intent in additives that can increase the viscosity of carbon dioxide at reservoir condition. This can in principle be achieved by addition of polymers as long as they are soluble in carbon dioxide. Beckman and coworkers have explored this area and reported that styrene / fluoroacrylate copolymers (Huang et. al., 2000), semi-fluorinated trialkyltin and fluorinated telechelic ionomers (Shi et. al., 2001b) may function as viscosity-enhancing agents for CO_2.

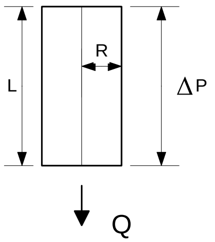
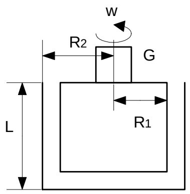
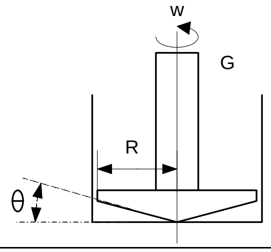
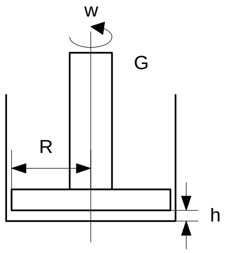
3.3 Viscosity of polymer melts containing SCFs at high pressure

There is continuing interest in lowering the viscosity of polymer melts in extrusion and molding operations. Increasing the temperature would lower the viscosity but is not always an option due to the thermal degradation. Therefore, reduction of viscosity of polymer melts is of great interest in polymer processing. Generally, the high viscosity of polymer melts is not favorable in the processing. Addition of CO_2 to polymer melts can reduce the viscosity, and also suppress the glass transition temperature and / or the melting temperature.

Royer and coworkers (Royer et. al., 2000) measured the rheology of polystyrene melts plasticized by CO_2 using a high-pressure extrusion die slit rheometer. Up to 80 % reduction in viscosity was observed. They also reported on the rheology and viscosity reduction of poly (methyl methacrylate), polypropylene, low-density polyethylene, and poly (vinylidene fluoride) with dissolved CO_2 at pressures up to 30 MPa (Royer et. al., 2001). Using a magnetically levitated sphere rheometer, rheology of PDMS melts plasticized by CO_2 was determined (Royer et. al., 2002). The results show that the polymer melt viscosity reduction reached two orders with a 30 % CO_2 addition.

Lan and coworkers studied the rheological behavior of polypropylene/CO_2 system at high pressure up to 60 MPa using a modified extrusion die slit viscometer (Lan and Tseng, 2002). The range of shear rate can be controlled in this viscometer. The viscosity of the polymer melts decrease significantly with addition of CO_2 at low shear rates. However, the viscosity reduction diminishes as shear rate increases. More recent, viscosity reduction efforts have been explored by Baird and coworks (Bortner and Baird, 2004).

Table 3.1 Summary of available viscometers

Viscometer	Schematic Diagram	Working Equations	Characteristics	Application range
Capillary Viscometer		$\Delta P = 8L\mu Q / \pi R^4$	No need for density data, but Reynolds number should be lower than 2100..	Low-viscosity, solvents, dilute solutions
Rotational Viscometer (coaxial cylinder)		$\eta = \dfrac{G}{2\pi L w}(\dfrac{1}{R_1^{\ 2} - R_2^{\ 2}})$	Controllable shear rate. Hard to load polymer and to control pressure.	High viscosity medium, polymer melts
Rotational Viscometer (cone-plate)		$\eta = \dfrac{3G}{2\pi R^3 w}\theta$	Controllable shear rate. Easy to load polymer.	High viscosity medium, polymer melts
Rotational Viscometer (rotating disk)		$\eta = \dfrac{2Gh}{\pi R^4 w}$	Controllable shear rate. Easy to load polymer.	High viscosity medium, polymer melts

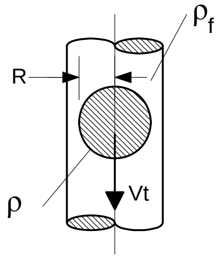
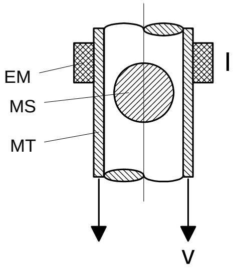
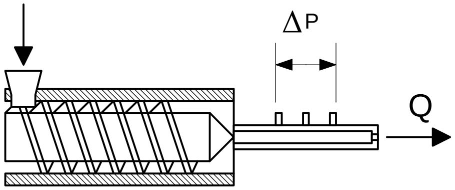
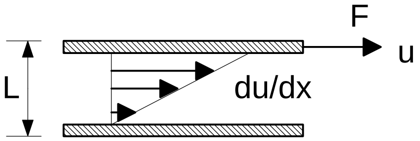
Falling/rolling-body Viscometer		$\eta = (2/9)(\rho - \rho_f)gR^2/V_t$	Need density measurement, shear rate cannot be controlled.	Low viscosity medium, dilute polymer solutions
Magnetoviscometer	A modification for falling/rolling body viscometer	N/A	Replace gravity field in falling/rolling body viscometer by controllable magnetic field.	Low and high-viscosity measurements
Magnetically Levitated sphere Rheometer		$\eta = \dfrac{K(I - I_0)}{v}$	Operate at constant pressure, at all concentration range from pure polymer to polymer/SCF solution, with controllable shear rate	Low and high-viscosity measurement
Extrusion Slit Die Rheometer		$\eta_{app} = \dfrac{\tau_w}{\dot{\gamma}_{app}}$, $\tau_w = \left(\dfrac{-\Delta P}{L}\right)\dfrac{H}{2}$, $\dot{\gamma} = \left(\dfrac{6Q}{wH^2}\right)$	Controllable shear rate.	High-viscosity measurements, especially suitable for polymer melts.
Sliding-plate Viscometer		$\eta_{app} = \dfrac{\tau_w}{\dot{\gamma}_{app}}$	Controllable shear rate.	High-viscosity measurement.

Table 3.2 Literature data for polymer solution viscosity at high pressures. (Polymer solutions with the solvent as the main component)

Systems	Temperature and pressure range	Viscosity range (mPa·s)	Reference
PDMS + cyclohexyl bromide	298-318 K, 1-40 MPa	0-3000	Kubota and Ogino, 1979
PS + *trans*-decahydronaphthalene	283-289 K, 1-100 MPa	10-1000	Wolf et. al., 1979
PS + *tert*-butyl acetate	274.8-403 K, up to 400 MPa	1-100	Schmidt and Wolf, 1982b
PS in THF, Zinc sulfonated PS (ZnSPS) in THF, poly (styrene-4-vinylpyridine) (PSVP) copolymer in THF, ZnSPS/PSVP in THF	295.2 K, up to 2000 MPa	$500\text{-}10^6$	Cook et. al., 1992a
PS in THF, PS in chloroform, (PIB) in THF, and partially hydrolyzed polyacrylamide (HPAM) in 2 % NaCl-water	295.7 K, up to 2000 MPa	$0\text{-}10^7$	Cook et. al., 1992b
PS + n-Butane	395-445 K, up to 70 MPa	0.10-0.30	Kiran and Sen, 1993
PE + n-Pentane	398-428 K, 20-60 MPa	0.10-0.60	Kiran and Gokmenoglu, 1995; Dindar and Kiran, 2002
PDMS + CO_2	300-460 K, up to 60 MPa	0.05-0.12	Xiong and Kiran, 1995; Dindar and Kiran, 2002
PS + n-hexane	323-423 K, up to 60 MPa	0.10-0.30	Xiong and Kiran, 1997
LDPE + Ethene	410-468 K, up to 140 MPa	30-50	Horst et. al., 1998
PS + Methylcyclohexane	340-400 K, up to 35 MPa	0.30-4.00	Yeo and Kiran, 1999
PS + Toluene + CO_2	320-360 K, up to 35 MPa	0.80-2.00	Yeo and Kiran, 1999a,b
Styrene/Fluoroarylate copolymer + CO_2	295 K, 6.7-48.3 MPa	Up to 3 η_{CO2} *	Huang et. al., 2000
Semi-Fluorinated Trialkyltin Fluorides + CO_2, Fluorinated Telechelic Ionomers + CO_2	297 K, 34 MPa	Up to 250 η_{CO2} *	Shi et. al., 2001
LDPE + Ethylene	223-463 K, up to 160 MPa	5-400	Kinzl et. al., 2003

* The relative viscosities to CO_2 were measured instead of the absolute viscosity.

Table 3.3 Literature data for polymer solution viscosity at high pressures. (Polymer solutions with the solutes (polymers) as the main component)

Systems	Temperature and pressure range	Viscosity range (Pa·s)	Reference
PS + CO_2	473 K, up to 20 MPa	1000-100000	Royer et. al., 2000
PMMA, PP, LDPE, PVDF	523 K, up to 30 MPa	1000-100000	Royer et. al., 2001
PDMS + CO_2	303 K, up to 30 MPa	40-60	Royer et. al., 2002
PP + CO_2	458-483 K, up to 60 MPa	800-2000	Lan and Tseng, 2002
Poly (propylene glycol) + CO_2 Poly (propylene glycol) + Fumed Silica + CO_2	298-308 K, Up to 5.5 MPa	1-100	Flichy et. al., 2005