CHAPTER II
EXPERIMENTAL

2.1 Materials

2.1.1 Polymers

The polymers used for this investigation were polyacylamides (PAM) and 70% hydrolyzed polyacrylamide (70% HPAM). The formers were purchased from Polyscience, Inc. (Catalog no. 22581, no. 19901, no. 02806 and no. 18522). The quoted molecular weights for these polymer, are 1×10^4, 7×10^5, $5-6 \times 10^6$ and 1.8×10^7, respectively. The 70%HPAM was purchased from Scientific Polymer Product, Inc. (catalog no. 377) with a quoted molecular weight of 200,000.

2.1.2 Solvents and other Chemicals

Sterile water was purchased from Government Pharmaceutical Organization. This water was used in order to make sure that there was minimum dust particles or ions in samples.

Sodium Chloride (NaCl, analytical grade) was purchased from Ajax chemicals. It was used to vary solution ionic strength.

Sodium Azide was purchased from the Clyde Industries Ltd. and used to prevent the growth of microorganisms.

2.2   Instruments

2.2.1 Rheometric Fluid Spectrometer

The system consisted of the Advance Rheometric Expansion System (ARES) from Rheometric Scientific, Inc., the homemade double couette cell, the homemade single couette cell and a constant temperature bath controller.

There were 2 transducers provided with the fluid rheometer (ARES); the transducer number 1 has a torque range of 0.004 to 10 gmf.cm and the transducer number 2 has a torque range of 0.04 to 100 gmf.cm

The homemade single couette cell consisted of a cup with an inside diameter of 47.9 mm and a bob with a diameter of 40.0 mm and a height of 40.0 mm. In order to measure the torque, the cylinder bob tube was connected to an upper parallel plate with a diameter of 25.0 mm which was attached to the transducer as shown in figure 2.1. This couette cell was named SCU.

The homemade double couette cells consisted of double cups with 4-changeable-inner cylinders and a hollow bob. Similar to the single couette cell, the bob was connected to the upper parallel plate with a diameter of 25.0 mm which was attached to the transducer. The designed apparatus is shown in figure 2.2. These couette cell units were named DCU-A, B, C, D. Their dimensions are tabulated in Table 2.1.

All SCU and DCU's were machined from plexiglass. The dimensions of these couette devices were determined by considering the maximum Reynolds number at the highest motor speed (Appendix A). To keep the temperature of the fluid constant, the temperature bath controller was used to control temperature over the range of 10 to $110^{\circ}C$.
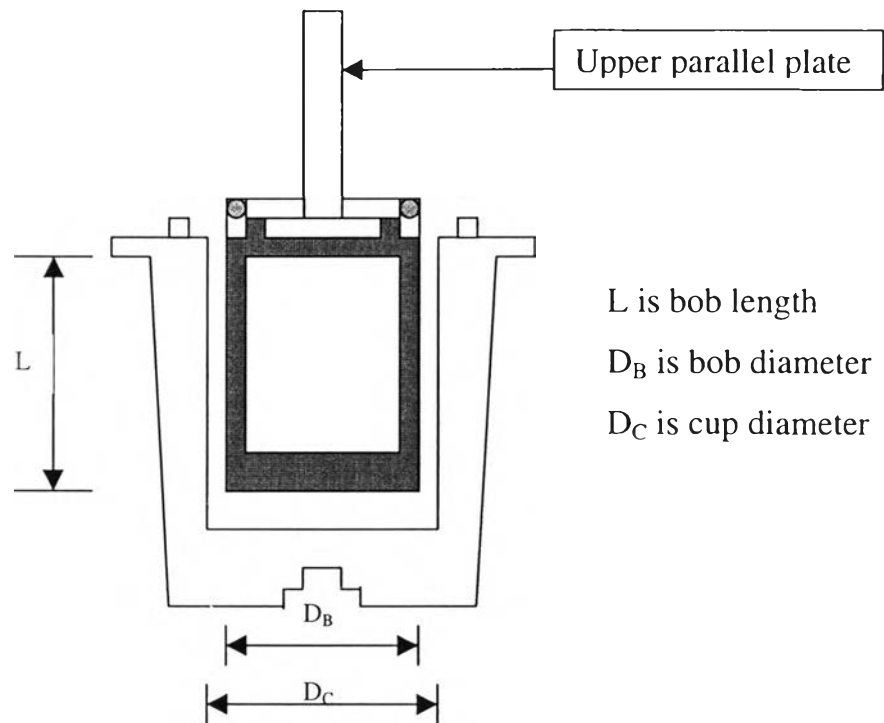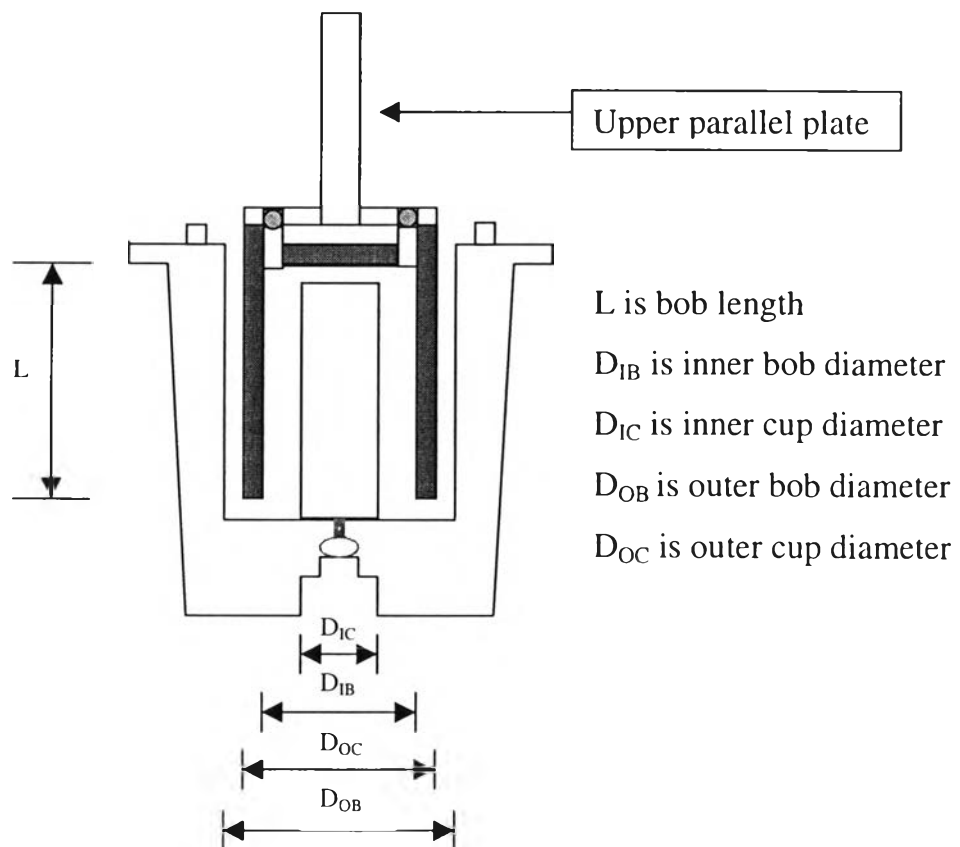
Figure 2.1 Assembly of the single couette cell unit (SCU).

L is bob length

D_B is bob diameter

D_C is cup diameter

Figure 2.2 Assembly of the double couette cell unit (DCU).

L is bob length

D_{IB} is inner bob diameter

D_{IC} is inner cup diameter

D_{OB} is outer bob diameter

D_{OC} is outer cup diameter

Table 2.1 Geometry of couette cell unit (CCU).

	DCU-A	DCU-B	DCU-C	DCU-D
D_{IC} (mm)	14.4	18.0	21.6	25.2
D_{IB} (mm)	36.1	36.1	36.1	36.1
D_{OB} (mm)	40.0	40.0	40.0	40.0
D_{OC} (mm)	47.9	47.9	47.9	47.9
L (mm)	40.0	40.0	40.0	40.0

2.2.2 Light Scattering Instrument

The laser light scattering instrument is the system model 4700 from Malvern instrument Ltd.. The system has seven separated units which consist of computer (NEC 16I), PCS100 spectrometer, correlator, temperature controller/power supply (PCS8), stepper motor controller (PCS7), pump/filter unit (RR98) and a 2 W Ar-Ion laser power supply.

2.2.3 Capillary Viscometer

(a) Ubbelohde Viscometer

The Cannon-Ubbelohde viscometers, no: B777; capillary size 50 was used to measure the viscosity of the samples at 30°C. It was obtained from Curtis Matheson Scientific, Inc.. Its specifications are as follow:

Size 50, no. B777, K (by manufacturer) = 0.004070 CSt/sec,

Viscosity range 0.3 to 1.6 CSt.

b) Water Bath and Thermostat

Digital thermostat model DT-2 with temperature resolution of ±0.1°C from Heto, Denmark was used to control temperature. The operation temperature range was from an ambient temperature to 110°C. The homemade transparent water bath was used. One side of water bath was made from glass.

The other side were made from stainless steel and covered with glassfiber to maintain a constant temperature.

(c) Timing device

A stopwatch was used in the experiment to provide the reading with a resolution of ±0.01 second.

2.2.4 Centrifugation

High speed centrifuge (ALC model PM180R) from ALC International Co. Ltd. was used to centrifuge the solution. The maximum speed is 12,000.

2.2.5 Refractometer

Optilab DSP Interferometric Refractometer was used to measure the refractive index increment (dn/dc_p) of polymer solution at a temperature of $30^{\circ}C$.

2.3 Methodology

2.3.1 Sample Preparation

Polymer was accurately weighed into an Erlenmeyer flask. Then a part of the solvent containing 0.02 wt% NaN_3 was added and the solution was stirred gently by a magnetic stirring machine for 1 day until all the polymer was dissolved. Then, the solution was placed into a suitable volumetric flask and the rest of the solvent was added until the exact volume of solution was obtained. The flask was capped and agitated gently for at least 4-10 days depending on molecular weight to make a uniform stock solution. This stock solution was diluted to the designated concentrations. All diluted solutions were filtered through Millipore membrane filters (pore sizes used were 0.2, 0.45 or 0.8 μm, depending on concentration and molecular weight).

In case of dilute solutions for light scattering measurement, the solutions were clarified by centrifugation for 1 hour at 8000 rpm. They were then collected from the middle part of the tube by using a dry clean syringe and passed through Millipore membrane filters (0.2, 0.45, 0.8 μm) before measurement.

2.3.2 Static Light Scattering Measurement

(a) *Principle*

The intensity data have been analyzed by using the classical Rayleigh-Gans-Debye equations (Young and Lovell,1992):

$$\frac{Kc}{\overline{R_\theta}} = \frac{1}{M_w P(\theta)} + 2A_2 c_p + 3A_3 c_p^2,$$
(2.1)

where M_w is the weight average molecular weight, $\overline{R_\theta}$ is the Rayleigh ratio for the solution, A_2 and A_3 are second and third virial coefficients, which quantify any interaction between solvent and molecule, and intramolecular interaction respectively, c_p is the solution concentration, and K is the optical constant, which is defined by:

$$K = \frac{4\pi^2 n_0^2 (dn / dc_p)^2}{\lambda^4 N_A},$$
(2.2)

where n_o is the refractive index of the solvent, dn/dc is the refractive index increment, λ is the wavelength, N_A is an Avogadro's number. The Rayleigh ratio is found by measuring the scattering from a sample solution. The Rayleigh ratio required is actually that for sample alone, so a sample of solvent is measured alone and subtracted from the solution scattering.

$$\overline{R_\theta} = R_\theta(\,solution\,) - R_\theta(\,solvent\,),\tag{2.3}$$

where R_θ is the Rayleigh ratio, the ratio of the scattered light intensity per unit volume of the scattering solution, per unit solid angle of the detector, to the incident light intensity (I_o) (Campbell and White, 1989).

The quantity $P(\theta)$ is called the form factor. For a random coil $P(\theta)$ is expressed by :

$$P(\theta) = 1 - q^2\,\frac{R_g^2}{3} + ...,\tag{2.4}$$

and hence

$$\frac{Kc_p}{R_\theta} = \frac{1}{M_w}(1 + \frac{q^2 R_g^2}{3})(1 + 2A_2 + ...) ,\tag{2.5}$$

where q is the scattering wave vector which can be defined as $q = 4\pi\sin(\frac{\theta}{2})/\lambda$. The equation (2.5) is the basis of the well-known Zimm plot analysis of light scattering data, in which Kc_p/R_θ is plotted versus $sin^2\theta/2 + kc_p$ where k is an appropriate graphical constant chosen to create a two-dimensional spread of angle-dependent light scattering data at specified concentrations on grid. Originally this grid is used to extrapolate each concentration set to zero angle, and each angle for all concentrations to zero concentration, then extrapolates the extrapolated lines to 0 angle and concentration where $Kc_p/R_\theta = 1/M_w$.

(b) *Procedure*

The static light scattering measurements were made by a Malvern 4700 spectrometer. The light source was Ar-Ion laser operating at a wavelength of 514.5 nm with the output power of 2 W. The aperture was set

at 500 μm. The measurements were performed at a temperature of 30°C, using toluene as a reference standard solution to calibrate the intensity scattered by the solution ($R_\theta(solution) = \dfrac{i_\theta(solution)}{i_\theta(solvent)} \times R_\theta(solvent)$). The large burchard cells (PCS 10) were used. The scattering intensities were investigated over the angular range of $75°<\theta<120°$ with 10 numbers of angle and were analyzed by Zimm plots to determined molecular weight and R_g. The measurement times were 10 seconds divided into 10 sub-scans.

2.3.3 Dynamic Light Scattering Measurement

(a) *Principle*

In dilute solution, the normalized intensity-intensity correlation function, $g^{(2)}(t)$, is an exponential decaying function, from which the diffusion coefficient may be derived through the Seigert relation with the electric field correlation function, $g^{(1)}(t)$:

$$g^{(2)}(t) = B(1 + \beta |g^{(1)}(t)|^2),\qquad(2.6)$$

where B is the baseline t is the delay time and β is a nonideality factor accounting for deviation from ideal correlation (Brown, 1993). For polydisperse system, $g^{(1)}(t)$, the first-order normalized electric field correlation function, is related to the normalized characteristic linewidth distribution function, $G(\Gamma)$ by the Laplace integral equation:

$$g^{(1)}(t) = \int G(\Gamma)\exp(-\Gamma t)d\Gamma,\qquad(2.7)$$

where $G(\Gamma)$ is the normalized distribution function of the decay rates.

The correlation data are analyzed by using the method of monomodal. The monomodal intensity autocorrelation functions, which only slightly deviate from a single exponential, are analyzed by fitting to a cumulant expansion. The cumulant method assumes nothing about the distribution form. The measured correlation function is simply fit a polynomial to the *LOG* of the normalized correlation function. Cumulant expansion refers to the full measured correlation function being represented by a theoretically infinite series each term representing a statistical moment of successively higher order. In principal these can be interpreted as giving information about the shape of the distribution of decay times and hence particle sizes. Generally the series to only 2 or 3 terms are truncated and we use the 1st moment to derive a z-average diffusion coefficient and the 2nd moment (polydispersity) to measure the width of the distribution.

$$LOG\left(\frac{G_2(t)}{B} - 1\right) = -2\Gamma t + \frac{2\mu_2}{2!\Gamma^2}(\Gamma t)^2 - \frac{2\mu_3}{3!\Gamma^3}(\Gamma t)^3 + ., \qquad (2.8)$$

where B is baseline and the first moment, Γ can be related to the translational diffusion coefficient, D_{app}:

$$D_{app} = \frac{\Gamma}{q^2}, \qquad (2.9)$$

where $q=(4\pi n_o/\lambda)sin\theta/2$, q is the magnitude of the scattering vector, λ is the wavelength of the incident light in a vacuum , n_o is the refractive index of solvent and θ is the scattering angle. The second moment, μ_2 is the variance in Γ which is defined as $\mu_2 = <\Gamma^2> - \overline{\Gamma}^2$ and is a measure of the width of the distribution. The third moment, μ_3 is a measure of the departure from symmetry of the distribution (skewness). The relation between the apparent translational diffusion coefficient and the center of mass diffusion coefficient can be written as:

$$D_{app} = D_{cm}(1 + f_c R_g^2 q^2),$$ (2.10)

where f_c is a dimensionless number. To avoid the problems from large particles, the measurement is performed by plotting D_{app} vs. q^2 and extrapolated to $q^2=0$ to get the center of mass diffusion coefficient which has a concentration dependence of:

$$D_{cm} = D_o(1 + k_d c_p + ...),$$ (2.11)

where k_d is the concentration dependence coefficient, D_o is the mutual diffusion coefficient at infinite dilution and D_{cm} is the value at concentration c_p.

Measurements from dynamic light scattering give the apparent hydrodynamic radius ($R_{h,app}$). When $R_{h,app}$ is extrapolated to zero polymer concentration, R_h can be related to the hydrodynamic friction constant. Using Stokes-Einstein relation, R_h is evaluated from the diffusion coefficient at infinite dilution, D_o:

$$R_h = \frac{k_B T}{6\pi\eta_s D_o},$$ (2.12)

where k_B is the Boltzman constant, T is the absolute temperature, η_s is the viscosity of the solvent.

(b) *Procedure*

Dynamic light scattering measurements were performed by Malvern 4700 spectrometer operating at a wavelength of 514.5 nm with an output power of 400 mW at the scattering angle between 75 to 110. The photomultiplier aperture was set at 200 μm. The autocorrelation functions of the scattered light intensity were analyzed in the monomodal mode. The 10

mm round quartz cells (RR84) were used and the samples were thermostatted during the measurement at a temperature of 30°C.

2.3.4 Viscosity Measurement

(a) *Principle*

Viscosity measurement can provide information on average chain dimensions, excluded volume effects governed by specific polymer-solvent interaction and chain stiffness. The basic viscosity parameters are shown below.

The kinematic viscosity, v, is obtained from the measured flow time, t, multiplied by the calibration constant, K:

$$v = Kt.$$ (2.13)

The dynamic viscosity, η, is calculated from the kinematic viscosity multiplied by the density of the solution:

$$\eta = v\rho,$$ (2.14)

where η is dynamic viscosity (centipoise or mPa.sec), ρ is the density of the solution (g/ml), and v is the kinematic viscosity (centistoke or mm^2/sec).

The degree to which the viscosity of solvent is enhanced by the addition of polymer can be expressed by the specific viscosity η_{sp}, defined by:

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s},$$ (2.15)

where η and η_s are the solution and solvent viscosity, respectively. The reduced viscosity $\eta_R = \eta_{sp}/c_p$ describes the change in the specific viscosity with polymer concentration c_p. A general expression for the change in reduced viscosity with the concentration of polymer can be developed as series expansion of η_R in c_p from the Huggins equation (Campbell and White, 1991).

$$\eta_R = \frac{\eta - \eta_s}{\eta c_p} = [\eta] + k_H [\eta] c_p + \ldots , \qquad (2.16)$$

where the coefficients are identified as $[\eta]$ is the intrinsic viscosity and k_H is the Huggins coefficient.

The molecular weight dependence of the intrinsic viscosity for a given polymer-solvent system is determined by using the Houwink-Mark-Sakurada (HMS) equation.

$$[\eta] = KM_v^a , \qquad (2.17)$$

where K and a values are constant for a given polymer, solvent at particular temperature. For polyacrylamide in water at 30°C, a and K values are given in Table 2.1 (Kurata and Tsunashima, 1989).

Table 2.2 a and K values of polyacrylamide in water at 30°C.

mole wt. Range($M*10^{-4}$)	$K*10^3$ (ml/g)	A
< 50	6.31	0.80
< 20	68	0.66
< 127	6.5	0.82

(a) *Procedure*

The experimental procedure involved introducing filtered solution in the lower bulb of the viscometer via the filling tube. The viscometer was then mounted vertically in water bath thermostat and left to equilibrate at the temperature of 30°C. The solvent was drawn up the central capillary tube by suction until it was above the upper etched mark. The time for solution to flow between two etched marks was determined.

2.3.5 Drag Reduction Measurement

(a) *Principle*

The experiments were carried out on the homemade couette cell in steady state mode. Laminar flow was assumed to occur in the single couette cell due to the stability of the flow by the centrifugal force whereas both laminar flow and turbulent flow occurred in the double couette cell. In double couette cell, the laminar flow occurred in the outer bob while the turbulent flow occurred in the inner bob. From a series of measurement of both angular speed of rotating cup and the torque applied to the stationary bob of both single couette cell and double couette cell, the inner wall shear stress can be calculated as:

$$\tau_{inner} = (M_{total} - M_{outer})K_\tau, \tag{2.18}$$

where τ_{inner} is inner wall shear stress, M_{total} is total torque measuring from double couette cell, M_{outer} is outer torque measuring from single couette cell and K_τ is stress constant which is expressed by (Ares instrument manual, 1995):

$$K_{\tau} = \frac{1000G_{c}}{2\pi L(R_{IB})^2},$$ (2.19)

where G_c is gravitational constant which is equal to 980.7 cm/s^2, L is length of bob (mm) and R_{IB} is inner radius of bob (mm).

The inner shear strain rate is given by:

$$\dot{\gamma} = \dot{\theta}K_{\gamma},$$ (2.20)

where $\dot{\gamma}$ is shear strain rate, $\dot{\theta}$ is angular velocity of motor and K_{γ} is strain constant which is expressed by:

$$K_{\gamma} = \frac{2}{((R_{IB}/R_{IC})^2 - 1)},$$ (2.21)

where R_{IC} is inner radius of cup (mm).

The experimental data, inner shear stress (τ_{inner}) and angular velocity ($\dot{\theta}$), were converted to Reynolds number (Re) and friction factor (f) using equations (2.22) and (2.23) which were defined for the couette cell as (Prima and Swinney,1985):

$$Re = \frac{\dot{\theta}R_{IC}(R_{IB} - R_{IC})}{v},$$ (2.22)

$$f = \frac{2\tau_{inner}}{\rho(\dot{\theta}R_{IC})^2},$$ (2.23)

where v is kinematic viscosity and ρ is density of solvent.

(b) *Procedure*

The measurements were performed on the Rheometric Fluid Spectrometer in DCU-A and SCU geometry. Fluid was filled into the couette cell carefully in order to prevent bubble formation in the annulus of concentric cylinders, which was rotating independently about the axis. During the measurement, the 48 couette geometry and transducer number 1 were used. The unit was operated at 30°C in steady state mode with the maximum shear rate of 500 1/sec and the minimum shear rate of 1 1/sec. The time delay before measurement and the measurement time were set at 5 and 10 seconds, respectively.

2.3.6 Refractive Index Increment Measurement

The refractive index increment (dn/dc) of the polymer/solvent system is necessary prerequisite for the calculation of molecular weight. The measurements were carried out at the wavelength, λ = 488 nm and the temperature of 30°C. Figure 2.3 shows a linear plot to determine dn/dc_p for three polymers. The values of dn/dc_p are tabulated in Table 2.3.

Table 2.3 dn/dc_p of PAM-PS-19901, PAM-PS-02806 and 70 % HPAM-SPP-377 solutions at 30°C.

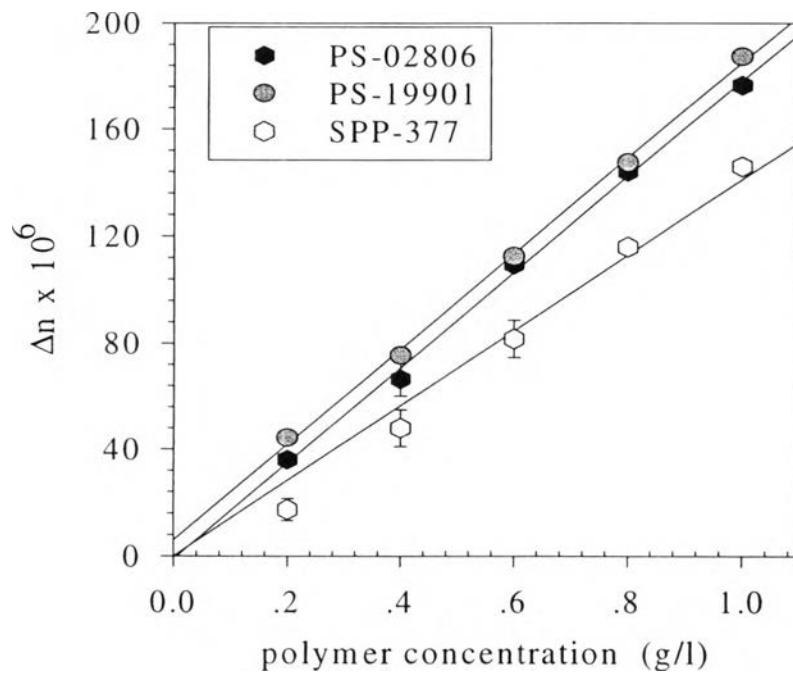| Sample	dn/dc_p (ml/g)
PAM-PS-19901 in water	0.179
PAM-PS-02806 in water	0.179
70%HPAM-SPP-377 in 0.02 M NaCl	0.144

Figure 2.3 Determination of *dn/dc_p* of PAM-PS-19901, PAM-PS-02806 and 70 % HPAM-SPP-377 solutions.