CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

2.1.1 Polymers

The commercial grade of hydroxypropyl cellulose (HPC) of 3 different molecular weights were purchased from the Aldrich Chemical, Inc. The weight average molecular weight (M_w) of HPC were 100,000, 370,000 and 1,000,000 as given by the supplier.

The analytical grade polystyrene latex beads were purchased from Sigma Chemical Company. Their diameters were 94, 302 and 460 nm, as given by the supplier.

2.1.2 Solvent and Other Chemicals

Thrice distilled deionized water (TDW) was used as the solvent in this study. It was purchased from the Government Pharmaceutical Organization. TDW was filtered through a Millipore GS 0.22 μm pore size membrane before using to remove dust particles.

Polyethoxylate (9.5) octylphenol or Triton x-100, a nonionic surfactant, was obtained from the Union Carbide (Thailand) Co., Ltd. with 100 % purity and used without further purification. Its molecular weight (M_w)

is 625 and critical micelle concentration (CMC) is 0.24 mM. (Edwards et. al, 1991).

Sodium azide (NaN_3) was used to prevent bacterial growth in HPC stock solution. It was purchased from Ajax Chemical Company, Inc.

2.2 Methodology

2.2.1 Purification Units

Centrifuge Machine

The high speed refrigerated centrifuge Model PM 180R from ALC International Co., Ltd. was used. The rotating head can be changed to obtain different speed and capacity. In this work, we used the rotating head no. A-H-12 with the maximum speed of 12,000 rpm (or 14,326 xg) and the maximum capacity of 38 ml x 8 bottles.

Filtering Accessories

A regular busher funnel with Whatman paper no.5 (pore size 2.5 μm) was used to remove dusts and large contamination. The borosilicate glass funnel and the fritted glass filter support with a membrane filter of pore size 0.45 μm were used to eliminate very tiny dusts. In case of HPC solutions, a micro-syringe filter with a membrane filter of pore size 0.22 μm was included as the last filtration step.

2.2.2 Sample Preparation

1) Preparation of the stock solution of polymer.

Three HPC fractions were obtained from Aldrich Chemical, Inc. The concentrated stock solutions were between 15-20 g/l. HPC were weighted out by a 4-digital weight balances and then dissolved in the triple deionized distilled water containing 0.02 % NaN_3 to prevent bacterial growth. The solutions were gently agitated by using a magnetic stirrer for at least 3 to 5 days for complete dissolution and allowed to settle for at least another 12 hours.

The stock solutions were then filtered through the paper filter no. 5 (pore size 2.5μm) from Whatman, and through the Millipore filter 0.45 μm for removing dust particles. For high molecular weight HPC (M_w=1,000,000), it was difficult to filter through the 0.45 μm membrane filter because of high viscosity so the stock solution was clarified by the no. 5 Whatman paper only.

2) Preparation of the polystyrene latex dispersion.

The latex bead content was 10 % as quoted by the supplier. In order to prepare 0.01 % wt. of the stock latex dispersions, the calculated weight of the three sizes of polystyrene latex were weighed out and filled with water until the total weight was equal to 100 g.

3) *Preparation of polystyrene latex in HPC solution.*

The stock solution was diluted by calculating the amount of the polymer stock solution to be added to the DDW, weighting using 4-digital weight balance, filling into a reagent plastic bottle and then adding the DDW until the total weight was equal to 100 g. The dilute solutions were shaken and allowed to settle overnight to reach the equilibrium. The HPC dilute solutions were filtered through a Millipore 0.45 μm membrane filter. For the measurement in only HPC solution, the centrifugation and filtering of the solution through the syringe with 0.22 μm Millipore membrane were required.

For the latex in HPC solution, the exact weight of latex and HPC was calculated. After adding the water of a specific amount, the mixture was shaken for 24 hours and allowed to stay overnight to reach the equilibrium. Before each measurement the sample was centrifuged at 7000 rpm for 25 minutes.

4) *Preparation of polystyrene latex in HPC solution in presence of Triton X-100.*

The calculated amounts of polystyrene latex and Triton x-100 were weighted out and then added to the water for the specific ratio. Shaking and allowing to stay overnight were required. After that, HPC solution was added later. All components were stored in a reagent plastic bottle and then shaked for 24 hours and allowed to settle for at least 12 hours for a well mixed condition.

2.2.3 Experimental Conditions

1) Conditions in viscosity measurement

For this measurement, the temperature was fixed at 30 °C controlled by a thermostat. For each measurement of HPC solution, it is necessary to filter the solution through the Millipore membrane 0.22 μm pore size before putting into the viscometer because dusty particles can affect the flow time. For the mixture between latex in HPC, there was no further filtration after mixing. The solutions were allowed in water bath for 15-20 minutes to achieve the thermal equilibrium before the measurement.

2) Conditions in light scattering measurement

The measurement temperature was fixed at 30 °C by a thermostat and the angle was settled at 90 degrees. The polymer solutions were carefully prepared to minimize the dust. The solutions were centrifuged at 7000 rpm for 25 minutes and then filtered through 0.20-0.45 μm membrane filters prior to inserting into the scattering cell. In case of the mixture containing latex spheres, filtration with Millipore membrane was not possible because the latex spheres could be removed out. Before making the measurement, the scattering cell was left in the light scattering unit for at least 20-25 minutes to achieve the thermal equilibrium.

2.3 Apparatus

2.3.1 Viscosity Measurement

Viscometer

Capillary viscometer is the simplest, most precise and most popular instrument for measuring viscosity.

Its measuring principle is based on the Poiseuille equation relating the time, t, necessary for volume, V, of a liquid to flow through a capillary with radius, r, and length, L, to the viscosity of the liquid, η, and the pressure difference, ΔP, between the ends of the capillary that is causing the flow:

$$t = \frac{8LV}{\pi r^4 \Delta P \eta} \; : \Delta P = \rho g h. \tag{2.1}$$

$$= \left(\frac{8LV}{\pi r^4 \Delta P \eta}\right)\left(\frac{\eta}{\rho}\right) = K\left(\frac{\eta}{\rho}\right). \tag{2.2}$$

Two sizes of Cannon-Ubbelohde viscometer were used. Both viscometers were supplied from Curtin Matheson Scientific Inc. which are illustrated in fig. 2.1. Their specifications are shown below.

1) Capillary size 50, no. 1067, Constant K= 0.004183 Cst/sec,
   Viscosity range : 0.8- 3.2 Cst
2) Capillary size 150, no. 209, Constant K= 0.033490 Cst/sec,
   Viscosity range : 7- 28 Cst

Figure 2.1 The Ubbelohde viscometer.

Principle

The time that liquid flows through a capillary from the upper mark to the lower mark is called the *effux time*, "t". When multiplied by a constant of the capillary, K, the **kinematic viscosity** , ν, is obtained as shown in following equation,

$$\nu = Kt, \qquad (2.3)$$

where K = the constant of each viscometer (Cst/sec)
t = the effux time (sec)

The dynamic viscosity, η is obtained by multiplying the kinematic viscosity by the density of the solution.

$$\eta = \nu\rho, \qquad (2.4)$$

where η = dynamic viscosity (CP or mPa.sec) where η = dynamic viscosity (CP or mPa.sec)

ρ = density (g/ml) at the same temperature of the viscosity measurement.

ν = kinematic viscosity (Cst or mm^2/sec)

Viscometric Funtions

Relative viscosity ***(η_r)*** is the ratio of the solution viscosity to the solvent viscosity, which is proportional for a first approximation in dilute solutions, to the ratio of the corresponding flow times. Then, the relative viscosity can be evaluated by an extremely simple relation:

$$\eta_r = \eta / \eta_s = \nu\rho / \nu_s\rho_s. \quad (2.5)$$

$$\cong t / t_s. \quad (2.6)$$

Specific viscosity ***(η_{sp})*** is the fractional increase in viscosity of the solution.

$$\eta_{sp} = (\eta_r - 1) / \eta_s = (\eta - \eta_s) / \eta_s. \quad (2.7)$$

$$= (\nu\rho - \nu_s\rho_s) / \nu_s\rho_s. \quad (2.8)$$

For dilute solution, ρ and ρ_s are nearly the same, so η_{sp} can be approximated as,

$$\eta_{sp} = (\nu - \nu_s) / \nu_s. \quad (2.9)$$

Reduced viscosity ***(η_R)*** is the quanlity in which concentration effect is not included and is defined as follows :

$$\eta_R = \eta_{sp} / C_p = (\nu - \nu_s) / C_p \quad , \qquad (2.10)$$

where η and η_s = dynamic viscosity of the solution and the solvent, respectively

ν and ν_s = kinematic viscosity of the solution and the solvent, respectively

ρ and ρ_s = density of the solution and the solvent, respectively.

C_p = concentration of polymer (% wt)

Both η_r and η_{sp} are dimensionless. As concentration increases, so does viscosity. Hence to eliminate concentration effects and to be in the dilute limit, the **intrinsic viscosity,** **[η]** is obtained by extrapolating η_R to zero concentration to give a dilute solution property.

Viscometric Accessories

Water bath with thermostat was used to control the temperature of the solution. The thermostat in this study was a digital model DT-2 with temperature stability ± 0.005 °C from Heto, Denmark. It can operate in the temperature range from an ambient temperature to 110 °C.

A stop watch was used to measure the flow time with a resolution of 0.01 second.

2.3.2 Dynamic Light Scattering Measurement

Principle

Dynamic light scattering (DLS) or quasielastic light scattering (QLS) is a relatively new method of measuring the diffusion coefficient in polymer solutions. It has many important advantages; eg. it is rapid and has a relatively high precision and only a small amount of samples is required. This technique is based on the dynamics of real-time fluctuations in the scattered light intensity which are recorded very rapidly by a specialized multichannel analyzer. The time required for the fluctuations to take place is the most important characteristic of the signal as the time series contains information about the dynamic properties of the polymer molecules.

In this work, the optical light source is Argon-Ion with the wavelength of 514.5 nm. The system consists of 8 units, they are a computer (NEC 16i), a spectrometer (PCS 100), a correlator (K7032-S), a temperature controller/power supplier (PCS 8), a stepper moter controller (PCS7), a pump/filter unit (RR98), a laser power supply (a-Spectra-Physics), and a printer. The DLS apparatus in this work was obtained from Malvern Instrument LTD., moael 4700 as shown in figure 2.2.

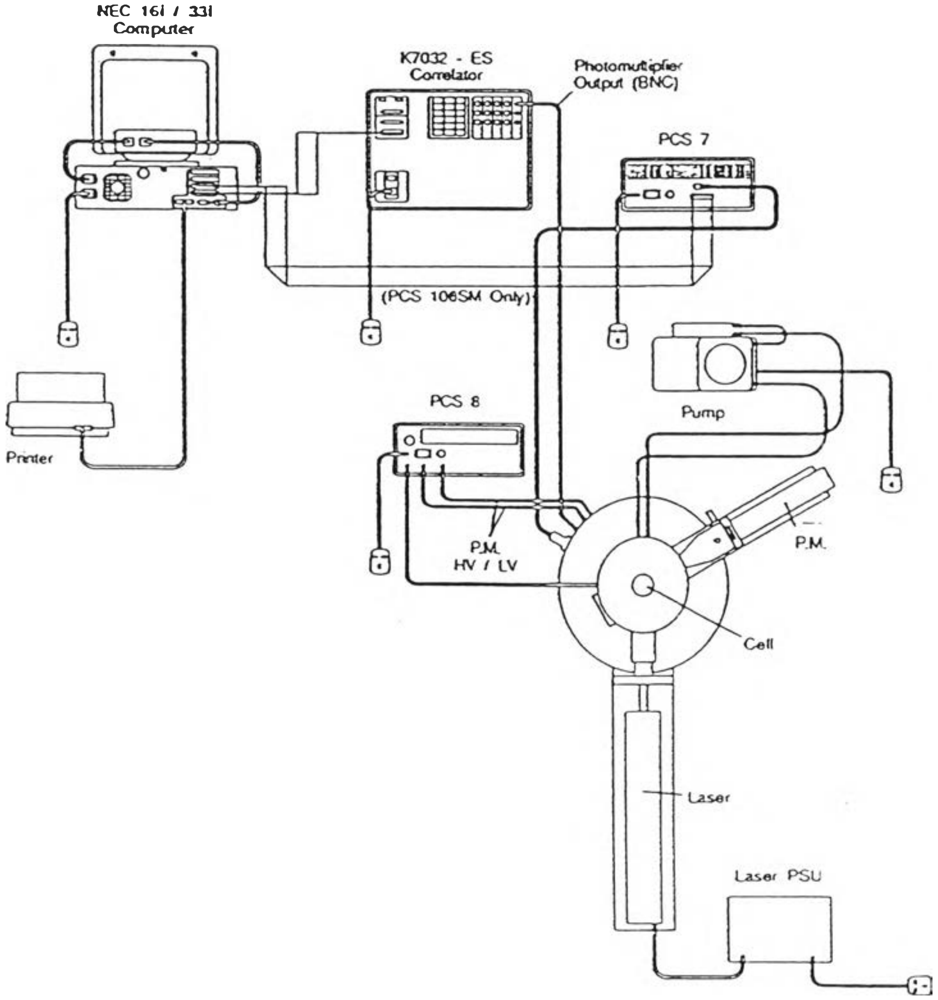

Figure 2.2 The schematic diagram of dynamic light scattering instrument (Malvern 4700).

Analysis

The analysis of light intensity may be carried out using either a spectrum analyzer or a correlator. In this experiment, we used the correlation technique where the correlation function is defined for a signal I(t) as

$$G_1(\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} I(t)I(t+\tau)dt. \qquad (2.11)$$

The normalized autocorrelation function of the field amplitude, g_1 (t) is given by

$$g_1(q,\tau) \equiv \frac{<E_S(q,0)E_S(q,\tau)>}{<|E_S|^2>} \equiv \frac{G_1(\tau)}{G_1(0)}, \qquad (2.12)$$

where τ is the correlation function delay time and q is the magnitude of the scattering vector, q which is defined as

$$q = (4\pi n/\lambda)\sin(\theta/2), \qquad (2.13)$$

where n is the refractive index of the solution, λ is the wavelength of light source in vacuum and θ is the scattering angle.

For a monodisperse system, the correlation function $g_1(\tau)$ is a simple exponentially decaying as a function of τ:

$$g_1(\tau) = \exp(-\Gamma\tau). \qquad (2.14)$$

Γ is the decay constant which can be expressed as

$$\Gamma = 1/T_q = D_t q^2, \qquad (2.15)$$

where T_q is the relaxation time (μsec).

The measured intensity correlation function $G_2(t)$ can be written as

$$G_2(t) = B(1+\beta|g_1(t)|^2), \qquad (2.16)$$

where $g_1(t)$ is the normalized correlation function related to the properties of the system investigated, b is the base line, and β is the coherence factor, which is generally considered as an adjustible parameter in the data analyzers procedure. It can be written in a normalized form as,

$$G_2(t) = G(t)/B = 1+\beta|g_1(t)|^2. \qquad (2.17)$$

For a polydisperse system, the analysis can proceed via the method of cumulants.

$$g_1(\tau) = A\exp(-\bar{\Gamma}\tau + \frac{1}{2!}\frac{\mu_2}{\bar{\Gamma}}(-\bar{\Gamma}\tau)^2 - \frac{1}{3!}\frac{\mu_3}{\bar{\Gamma}}(-\bar{\Gamma}\tau)^3 + \ldots). \qquad (2.18)$$

$$\ln g_1(\tau) = -\bar{\Gamma}\tau + \frac{1}{2!}\frac{\mu_2}{\bar{\Gamma}}(-\bar{\Gamma}\tau)^2 - \frac{1}{3!}\frac{\mu_3}{\bar{\Gamma}}(-\bar{\Gamma}\tau)^3 + \ldots, \qquad (2.19)$$

$$\text{where } \bar{\Gamma} = \int_0^\infty Q(\Gamma)d\Gamma = <D_t>_z q^2, \qquad (2.20a)$$

$$\mu_n = \int(\Gamma - \bar{\Gamma})^n Q(\Gamma)d\Gamma, \qquad (2.20b)$$

τ is the correlation time delay, $g(\tau)$ is the normalized correlation function, and $Q(\Gamma)$ is the distribution of Γ values.

The first cumulant, $\bar{\Gamma}$ represents the mean relaxation rate, Γ and the second cumulant or the variance of the relaxation rates with respect to the mean. The first cumulant is proportional to q^2, the proportionality factor representing the z-average of the diffusion coefficients as shown in eq.(2.15). Hydrodynamic radius, R_h can be determined using the Stokes-Einstein's equation :

$$D^0 = \frac{k_B T}{6\pi\eta_s R_h}, \tag{2.21}$$

where k is the Boltzmann's constant,

T is the absolute temperature,

and η_S is the solvent viscosity at temperature T.

The hydrodynamic radii of latex spheres can be estimated by DLS. Since latex particles scatter strongly, measurement may be carried out at a very low concentration. The measurements in a presence of polymeric component can be used to determine the effective thickness, δ, of the adsorbed polymer layer at the latex-solvent interface. To make such measurements, it is necessary to work at low concentration of polymer so that we can assume that the effect of the polymer-polymer interactions can be neglected. For a dilute solution of polymer, if the concentration of latex is very small, the viscosity of the solvent , η_s, is nearly the same as the solution viscosity, η. The measured diffusion is equivalent to the *translational diffusion coefficient*, D_t, which refers to the overall motion of a single latex particle in limit of small q value (qR<<1). In case of high concentration of polymer, D_c or *cooperative diffusion* is observed. D_c reflects the motion of strands of the size of the screening length, ξ. So in dilute solution, the observed diffusion is D_s and only single mode can be detected at qR<<1. In a semidilute solution, two modes are obtained: fast mode and slow mode. The former mode is referred to D_c and the latter mode is referred to D_{slow}.