

## CHAPTER IV

### EXPERIMENTS AND RESULTS

#### **4.1 Experimental Methods**

##### **4.1.1 Instrument Setup**

Several components comprise the photon correlation system, including (6):

- (1) the incident light source and its associated optics
- (2) the light scattering cell or sample cell and its temperature control electronics.
- (3) the detector and its associated optics
- (4) the electronic components associated with the detector

The block diagram of system setup is shown in Figure 4.1. The 50 mW He-Ne laser is used as a light source. It produces a continuous beam through the converging lens of focal length 15 cm. Laser beam is focused to the center of the sample cell that is placed inside the temperature control chamber. The heat reservoir of the temperature control chamber is made of brass and heated by the heating coil wrapped around the brass cylinder, at the top with a thermistor as shown in Figure 4.2. The resistance of the thermistor decreases while the temperature of the chamber increases. It is measured by the digital multimeter KEITHLEY

K-2000 that is connected to a microcomputer via an IEEE-488 communication port.

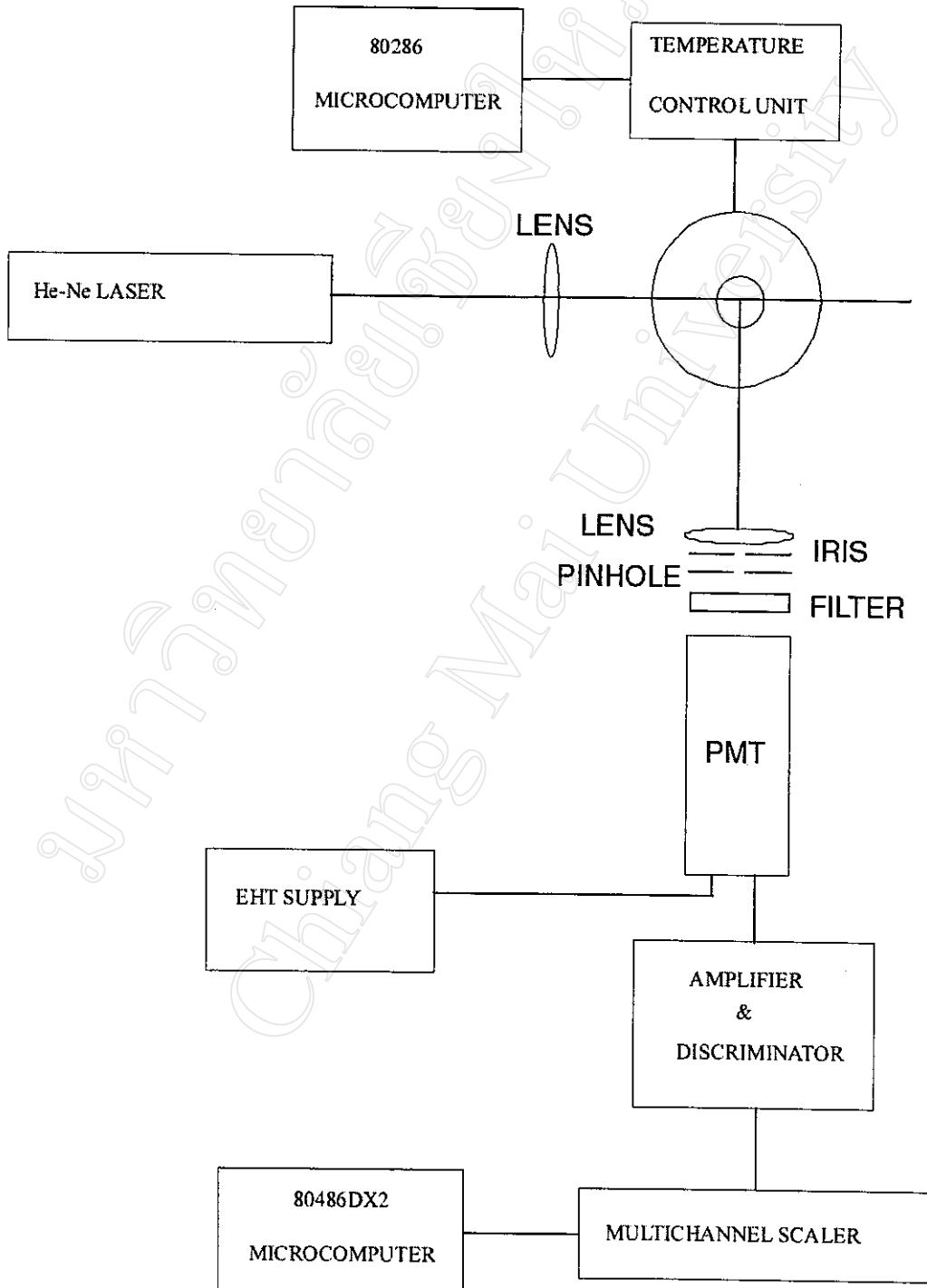


Figure 4.1 Block diagram of photon correlation experimental setup

The microcomputer uses the resistance value from the digital multimeter (DMM) and compares this with the setting point. It then sends the trigger signal to the switch of a power supply to heat the chamber if the temperature of chamber is lower than the setting point or to switch off the heater if the temperature of the chamber is higher than the setting point. The 8255 PC-plug-in card is used to interface the solid state relay.

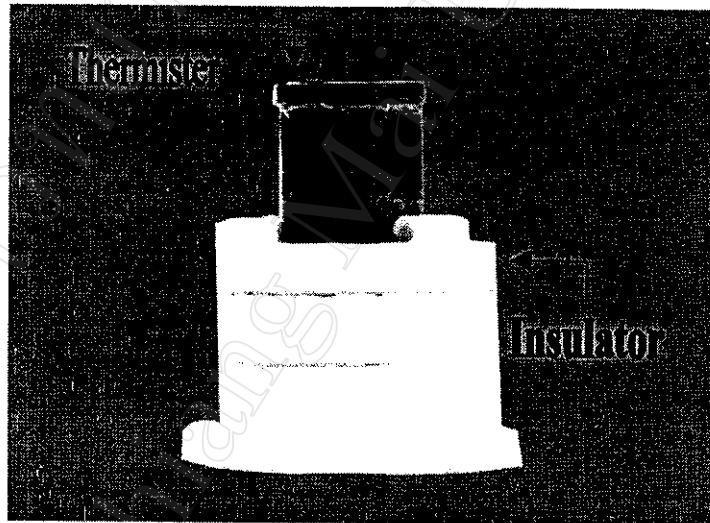


Figure 4.2 Temperature control chamber with insulator

The temperature control program is written in BASIC programming language. The calibration curve of temperature and resistance readings are required (see appendix A).

The PMT housing is placed on the standard optical spectrometer turntable. The scattering beam is brought to the photomultiplier tube through the lens system, 632.8 nm filter and pinhole (400 microns). This PMT has a high voltage power supply of 1750 V DC. Photon count signal from the PMT is passed to the amplifier and discriminator (Stanford research systems model SR445) for further amplification before sending to the multichannel scaler (EG&G ORTEC Turbo-MCS). The Turbo-MCS is connected to the microcomputer via Turbo-MCS-to-PC interface card. The delay time, number of loops (run), and the correlation data on files are controlled by the PC-software. This software is written with C language (see appendix B).

#### **4.1.2 Procedures**

1. Set up the equipment as in 4.1.1.
2. Place the optical cell in the temperature control chamber.
3. Set the temperature and wait for at least 4 hours before starting the measurement. Temperature of 37.2, 39.2, 42.4, 44.7, 47.2, and 49.8 °C were used in this experiment.
4. Turn on all units of light scattering system.

5. Run the computer program to form a correlation function of the photon counts. The number of runs used in this work was 4500 due to its weak. The correlation function was saved on diskette every 500 runs.

## 4.2 Data Treatment

### 4.2.1 Determination of translational diffusion coefficient

The treatment of data relies on the assumption that Equation 2.25 is appropriate for conditions studies. All correlation data are fitted for Equation

$$G^{(2)}(\tau) = A + B(\exp(-C\tau) + f \exp(-D\tau))^2 \quad (4.1)$$

where A, B, C and D are constants,

$$\text{and the fraction } f = \frac{c_2 I_2}{c_1 I_1}.$$

The intensity per unit concentration of polymer species 1 and sample 2 can be found from the average of photon counts of sample 1 and sample 2 respectively. The parameters C and D are:

$$C = D_1 K^2$$

$$\text{and } D = D_2 K^2$$

Therefore, we can find the diffusion coefficient of each species from

$$D_1 = C/K^2 \quad \text{and} \quad D_2 = D/K^2 \quad (4.2)$$

At 90 degrees of scattering angle as in this case;

$$K = \frac{4n\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) = \frac{4\pi(1.426)}{632.8 \times 10^{-9}} \sin\left(\frac{90}{2}\right)$$

such that  $K^2 = 4.0095 \times 10^{14} \text{ m}^{-2}$

#### 4.2.2 Determination of apparent translational diffusion coefficient

The correlation data are also forced to fit to a single exponential Equation.

$$G^{(2)}(\tau) = A' + B'(\exp(-C'\tau))^2 \quad (4.3)$$

where  $C' = \bar{\Gamma}$

$$\bar{\Gamma} = \bar{D}K^2$$

$$\text{and } \bar{D} = \frac{c_1 M_1 D_1 + c_2 M_2 D_2}{c_1 M_1 + c_2 M_2} \quad (4.4)$$

called the apparent diffusion coefficient.

We can compare the result from Equation 4.2 to Equation 4.4.

#### 4.2.3 Determination of the constant $k_D$

From the plot of diffusion coefficient D versus concentration we can determine the slope and from Equation 2.42

$$D = D_0[1 + k_D c] \quad (4.5)$$

Therefore, the slope of the graph can be written as

$$\begin{aligned} m_D &= D_0 k_D \\ k_D &= \frac{m_D}{D_0} \end{aligned} \quad (4.6)$$

The  $k_D$  can be derived from Equation 2.44;

$$k_D = 0.8A_2 M - \frac{N_A V_h}{M} - \bar{v} \quad (2.44)$$

where  $\bar{v}$  is the specific volume of polymer, and the polystyrene used has  $\bar{v} = 0.00095 \text{ kg.m}^{-3}$ .

#### 4.2.4 Determination of the friction constant

From the value of diffusion coefficient, we can find the value of  $\zeta$  by using the Einstein relation (Equation 2.39), at the temperature T

$$\zeta = \frac{k_B T}{D} \quad (4.7)$$

where  $k_B$  is the Boltzman constant =  $1.3805 \times 10^{-23}$  kg.m<sup>2</sup>.s<sup>-2</sup>.K<sup>-1</sup>

#### 4.2.5 Determination of the constant $k_\zeta$

From the graph of the frictional coefficient versus concentration and the Equation 2.41

$$\zeta = \zeta_0(1 + k_\zeta c) \quad (4.8)$$

The slope of the plot can be found to be

$$m_\zeta = \zeta_0 k_\zeta$$

and

$$k_\zeta = \frac{m_\zeta}{\zeta_0} \quad (4.9)$$

and from Equation 2.43

$$k_\zeta = 1.2 A_2 M + \frac{N_A V_h}{M} \quad (2.43)$$

#### 4.2.6 Determination of polystyrene sizes

From the Stoke-Einstein relationship, we can find the hydrodynamic radius of polystyrene from

$$a_h = \frac{k_B T}{6\pi\eta D_0} \quad (4.10)$$

where  $\eta$  is the viscosity of the solvent ( appendix C).

The hydrodynamic radius enables us to find the hydrodynamic volume

$$V_h = \frac{4}{3}\pi a_h^3 \quad (4.11)$$

#### 4.2.7 Determination of second virial coefficient $A_2$

We can determine the  $A_2$  from the Equation 2.45

$$A_2 = \frac{4N_A V_h}{M^2} \quad (2.45)$$

where  $N_A$  is the Avogadro's number =  $6.023 \times 10^{26}$  (kg.mole) $^{-1}$

### 4.3 Results

Each sample has two sharp fractions of different molecular weight polystyrene as shown in Table 4.1. The sample of photon correlation function is shown in Figure 4.3. The correlation function is force fitted to the Equation 4.3 and the results are shown in Table 4.2. Figure 4.4 shows the distribution of photon count from the photomultiplier tube. The average photon count from sample 1 and sample 2 per unit concentration are shown in Table 4.3, including the intensity ratio  $f$ . By using the intensity ratio  $f$  and Equation 4.1, we can force fit the correlation data of sample 3 to sample 7 which are the mixtures of two different molecular weight polystyrene in cyclohexane. The values of  $C$  and  $D$  at several temperatures are shown in Table 4.4 and 4.5 respectively. The apparent translational diffusion coefficients of all samples are shown in Table 4.6. The translational diffusion coefficient of  $M = 100000$  and  $M = 600000$  at several concentrations is shown in Table 4.7 and 4.8 respectively.

The relation of translational diffusion coefficient and concentration of  $M = 100000$  and  $M = 600000$  are shown in Figure 4.5 – 4.16. The constants  $D_0$ ,  $k_D$ ,  $a_h$ , and  $V_h$  are shown in Table 4.9 and 4.10 and their relation with temperature is shown in Figure 4.17 - 4.22. The friction constant  $\zeta$  of each molecular weight is shown in Table 4.11 and 4.12.

The relation between friction constant of  $M = 100000$  and  $M = 600000$  and concentration is shown in Figure 4.23 - 4.34. The constant  $\zeta_0$ ,  $k_\zeta$ , and second virial  $A_2$  are show in Table 4.13 and 4.14. By using Equation 4.4, we can find the apparent translational diffusion coefficient of 2 species of polystyrene in solution as shown in Table 4.15. Moreover, the constant  $k_D$  and the constant  $k_\zeta$  can be evaluated from theory as shown in Table 4.16.

Sample Number	$C_1$	$C_2$	$C$
	(mg/ml) For $M=100000$	(mg/ml) For $M=600000$	(mg/ml) Total concentration
1	10	0	10
2	0	2.0	2.0
3	5.0	1.0	6.0
4	3.5	1.3	4.8
5	6.5	0.7	7.2
6	1.5	1.7	3.2
7	8.5	0.3	8.8

Table 4.1 Fraction and total concentration of each sample.

Temperature (°C)	$\bar{\Gamma} \pm \Delta\bar{\Gamma}$						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
37.2	17461.3± 727.6	6457.1± 102.3	9342.3± 265.6	8687.7± 286.0	11321.9± 357.8	6925.5± 162.2	13670.7± 669.6
39.2	17615.2± 688.9	6754.2± 147.8	9575.0± 320.8	8903.0± 284.5	11544.3± 407.0	7091.4± 200.4	14344.0± 724.0
42.4	18316.7± 878.9	7339.0± 174.0	10405.7± 359.3	9702.2± 299.1	12392.7± 424.1	7572.4± 224.2	15467.3± 692.5
44.7	19013.6± 772.7	7524.4± 198.3	11234.5± 317.3	9868.1± 337.1	12998.3± 548.3	7812.0± 267.5	16225.1± 787.8
47.2	19875.3± 1049.5	8120.0± 187.5	11986.1± 442.9	10433.2± 382.9	13341.3± 600.7	8339.1± 293.4	16886.8± 1082.7
49.8	20463.1± 1104.7	8298.3± 163.8	12607.3± 579.3	11050.8± 401.2	13984.9± 605.9	8733.7± 290.1	17531.9± 957.3

Table 4.2  $\bar{\Gamma}$  from fitting with single exponential of each sample at several temperatures.

Temperature (°C)	Intensity (photon counts) per unit concentration							Fitting variable f (intensity ratio)						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
37.2	0.265	1.779	1.345	2.497	0.724	7.620	0.237							
39.2	0.291	1.592	1.092	2.029	0.588	6.190	0.193							
42.4	0.302	1.552	1.027	1.908	0.553	5.820	0.181							
44.7	0.280	1.700	1.213	2.254	0.653	6.876	0.214							
47.2	0.314	1.639	1.042	1.936	0.561	5.906	0.184							
49.8	0.273	2.144	1.569	2.913	0.845	8.889	0.277							

Table 4.3 Average photon count per unit concentration and the fraction f of each sample.

Temperature (°C)	C±ΔC				
	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
37.2	14361.7±1802.4	13473.4±2009.7	15230.7±2066.1	12310.4±1864.0	16451.1±2058.0
39.2	14920.7±1854.8	13842.3±1724.8	15662.1±1944.6	12771.4±1278.8	16872.4±2065.3
42.4	15351.2±1459.5	14600.8±2021.2	16301.7±1921.0	13430.0±1812.4	17501.0±1634.2
44.7	15907.3±1272.3	15077.1±2355.5	16800.1±1811.2	13902.8±1378.9	18003.1±2152.0
47.2	16750.2±1484.2	15551.0±1615.0	17348.7±1967.0	14352.7±1842.0	18575.6±1611.6
49.8	17562.4±1979.4	16042.3±1828.7	17854.2±1856.3	14862.4±1641.4	19078.2±2310.7

Table 4.4 Coefficient C from fitting the correlation data to Equation 4.1  
for samples 3-7.

Temperature (°C)	D±ΔD				
	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
37.2	5305.3±493.7	5647.2±326.8	4847.5±448.8	6160.8±359.9	4350.0±312.8
39.2	5512.1±503.9	6002.4±517.5	5301.2±421.6	6481.2±512.2	4748.2±317.6
42.4	6051.2±550.9	6511.2±438.9	5811.7±368.0	6922.0±565.3	5302.7±405.6
44.7	6524.3±413.3	6852.3±524.3	6135.1±380.2	7379.1±392.2	5660.0±395.6
47.2	7002.4±550.7	7271.8±357.3	6562.0±318.7	7712.3±397.3	6098.7±465.6
49.8	7522.4±492.1	7732.7±531.7	7042.2±365.2	8164.0±421.4	6557.4±375.4

Table 4.5 The coefficient D from fitting the correlation data to Equation 4.1  
for samples 3-7.

Temperature (°C)	$\bar{D} = \bar{\Gamma} / K^2 \times 10^{11} \text{ m}^2\text{s}^{-1}$						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
37.2	4.35498± 0.18147	1.61045± 0.02551	2.37992± 0.06624	2.19172± 0.07133	2.82377± 0.08924	1.70233± 0.04045	3.40958± 0.16700
39.2	4.39337± 0.17182	1.68455± 0.03686	2.38808± 0.08001	2.19554± 0.07096	2.82936± 0.10151	1.76865± 0.04998	3.57750± 0.18057
42.4	4.56833± 0.21920	1.83040± 0.04340	2.52044± 0.08961	2.44474± 0.07460	3.16566± 0.10577	1.88861± 0.05592	4.00731± 0.17275
44.7	4.74214± 0.19272	1.87664± 0.04946	2.67727± 0.07913	2.46118± 0.08407	3.44140± 0.13675	1.94837± 0.06672	4.04666± 0.19648
47.2	4.95705± 0.26175	2.02519± 0.04686	2.98943± 0.11046	2.55224± 0.09550	3.25260± 0.14982	2.15466± 0.07318	4.33640± 0.27003
49.8	5.10365± 0.27552	2.06966± 0.04085	3.34388± 0.14448	2.88086± 0.10006	3.48794± 0.15112	2.17825± 0.07235	4.37259± 0.23876

Table 4.6 The apparent translational diffusion coefficient of all samples.

Temperature (°C)	$D_1 = C / K^2 \times 10^{11} \text{ m}^2\text{s}^{-1}$				
	Sample 3 $C_1=5.0$	Sample 4 $C_1=3.5$	Sample 5 $C_1=6.5$	Sample 6 $C_1=1.5$	Sample 7 $C_1=8.5$
37.2	3.58192± 0.44953	3.36037± 0.50124	3.79865± 0.51530	3.07031± 0.46490	4.10303± 0.51328
39.2	3.72134± 0.46260	3.45238± 0.43018	3.90625± 0.48500	3.18528± 0.31894	4.20811± 0.51510
42.4	3.82871± 0.36401	3.64155± 0.50410	4.06577± 0.47911	3.34954± 0.45203	4.36488± 0.40758
44.7	3.96739± 0.31732	3.76034± 0.58748	4.19007± 0.45173	3.46746± 0.34391	4.49011± 0.53672
47.2	4.17763± 0.37017	3.87854± 0.40279	4.32690± 0.49059	3.57967± 0.45941	4.63290± 0.40195
49.8	4.38020± 0.49368	4.00107± 0.46298	4.45297± 0.46298	3.70680± 0.40938	4.75825± 0.57631

Table 4.7 Diffusion coefficient of polystyrene M=100000 in cyclohexane.

Temperature (°C)	$D_2 = D / K^2 \times 10^{11} \text{ m}^2\text{s}^{-1}$				
	Sample 3 $C_2=1.0$	Sample 4 $C_2=1.3$	Sample 5 $C_2=0.7$	Sample 6 $C_2=1.7$	Sample 7 $C_2=0.3$
37.2	1.32318± 0.12313	1.40845± 0.08151	1.20900± 0.11193	1.53655± 0.08976	1.08492± 0.07801
39.2	1.37476± 0.12568	1.49704± 0.12907	1.32216± 0.10515	1.61646± 0.12775	1.18424± 0.07921
42.4	1.50922± 0.13740	1.62394± 0.10947	1.44948± 0.09178	1.72640± 0.14100	1.32253± 0.10116
44.7	1.62721± 0.10308	1.70902± 0.13076	1.53014± 0.09482	1.84040± 0.09782	1.41165± 0.09867
47.2	1.74645± 0.17465	1.81364± 0.08911	1.63661± 0.07949	1.92351± 0.09909	1.52106± 0.11612
49.8	1.87614± 0.12273	1.92859± 0.13261	1.75638± 0.09108	2.03616± 0.10510	1.63547± 0.09363

Table 4.8 Diffusion coefficient of polystyrene M=600000 in cyclohexane.

Temperature (°C)	$D_{01} \times 10^{11} \text{ m}^2\text{s}^{-1}$	$k_D \times 10^{-3} \text{ m}^3\text{kg}^{-1}$	$a_H \times 10^{-8} \text{ m}$	$V_m \times 10^{-24} \text{ m}^3$
37.2	2.8349±0.0120	5.3011±0.0686	0.9730±0.0041	3.8592±0.0282
39.2	2.9716±0.0202	4.8427±0.1094	1.0131±0.0069	4.3551±0.0512
42.4	3.1291±0.0117	4.6061±0.0599	1.0973±0.0041	5.5343±0.0358
44.7	3.2343±0.0134	4.6036±0.0666	1.1559±0.0048	6.4684±0.0465
47.2	3.3397±0.0410	4.7176±0.1974	1.2127±0.0149	7.4709±0.1589
49.8	3.4785±0.0688	4.5435±0.3169	1.2438±0.0246	8.0594±0.2760

Table 4.9 Diffusion coefficient at zero concentration,  $k_D$ , hydrodynamic radius, and hydrodynamic volume of polystyrene M = 100000.

Temperature (°C)	$D_0 \times 10^{11} \text{ m}^2\text{s}^{-1}$	$k_D \times 10^3 \text{ m}^3\text{kg}^{-1}$	$a_{h2} \times 10^8 \text{ m}$	$V_{h2} \times 10^{-23} \text{ m}^3$
37.2	$0.9967 \pm 0.0102$	$3.1425 \pm 0.0853$	$2.7677 \pm 0.0284$	$8.8806 \pm 0.1580$
39.2	$1.0995 \pm 0.0150$	$2.7057 \pm 0.1113$	$2.7381 \pm 0.0374$	$8.5989 \pm 2.0356$
42.4	$1.2326 \pm 0.0116$	$2.3952 \pm 0.0755$	$2.7857 \pm 0.0261$	$9.0548 \pm 0.1470$
44.7	$1.3346 \pm 0.0168$	$2.1238 \pm 0.1006$	$2.8011 \pm 0.0353$	$9.2060 \pm 0.2013$
47.2	$1.4369 \pm 0.0099$	$2.0332 \pm 0.0549$	$2.8187 \pm 0.0195$	$9.3804 \pm 0.1123$
49.8	$1.5804 \pm 0.0256$	$1.6448 \pm 0.1271$	$2.7375 \pm 0.0443$	$8.5934 \pm 0.2408$

Table 4.10 Diffusion coefficient at zero concentration,  $k_D$ , hydrodynamic radius, and hydrodynamic volume of polystyrene  $M = 600000$ .

Temperature (°C)	$\zeta \times 10^{10} \text{ kg.s}$					
	Sample 1 $C_1=10$	Sample 3 $C_1=5.0$	Sample 4 $C_1=3.5$	Sample 5 $C_1=6.5$	Sample 6 $C_1=1.5$	Sample 7 $C_1=8.5$
37.2	$0.9838 \pm 0.0410$	$1.1961 \pm 0.1501$	$1.2750 \pm 0.1902$	$1.1279 \pm 0.1530$	$1.3954 \pm 0.2113$	$1.0442 \pm 0.1362$
39.2	$0.9815 \pm 0.0384$	$1.1587 \pm 0.1440$	$1.2490 \pm 0.1556$	$1.1039 \pm 0.1371$	$1.3537 \pm 0.1355$	$1.0247 \pm 0.1254$
42.4	$0.9536 \pm 0.0458$	$1.1378 \pm 0.1082$	$1.1962 \pm 0.1656$	$1.0714 \pm 0.1263$	$1.3005 \pm 0.1755$	$0.9980 \pm 0.0932$
44.7	$0.9253 \pm 0.0376$	$1.1060 \pm 0.0884$	$1.1669 \pm 0.1823$	$1.0472 \pm 0.1129$	$1.2654 \pm 0.1255$	$0.9772 \pm 0.1168$
47.2	$0.8922 \pm 0.0471$	$1.0586 \pm 0.0938$	$1.1402 \pm 0.1184$	$1.0221 \pm 0.1159$	$1.2354 \pm 0.1586$	$0.9546 \pm 0.0828$
49.8	$0.8736 \pm 0.0472$	$1.0178 \pm 0.1147$	$1.1143 \pm 0.1289$	$1.0012 \pm 0.1041$	$1.2027 \pm 0.1328$	$0.9370 \pm 0.1348$

Table 4.11 Friction constant of polystyrene  $M = 100000$  in cyclohexane.

Temperature (°C)	$\zeta \times 10^{10} \text{ kg.s}$					
	Sample 2 $C_2=2$	Sample 3 $C_2=1.0$	Sample 4 $C_2=1.3$	Sample 5 $C_2=0.7$	Sample 6 $C_2=1.7$	Sample 7 $C_2=0.3$
37.2	2.6604± 0.0421	3.2379± 0.3013	3.0419± 0.1760	3.5437± 0.3281	2.7883± 0.1629	3.9490± 0.2840
39.2	2.5597± 0.0560	3.1365± 0.2867	2.8803± 0.2483	3.2613± 0.2594	2.6676± 0.2108	3.6412± 0.2436
42.4	2.3799± 0.0564	2.8864± 0.2628	2.6825± 0.1808	3.0053± 0.1903	2.5233± 0.2061	3.2938± 0.2519
44.7	2.3382± 0.0616	2.6966± 0.1708	2.5675± 0.1965	2.8677± 0.1777	2.3842± 0.1267	3.1084± 0.2173
47.2	2.1837± 0.0504	2.5322± 0.1991	2.4384± 0.1198	2.7022± 0.1312	2.2992± 0.1184	2.9075± 0.2220
49.8	2.1541± 0.0425	2.3763± 0.1555	2.3117± 0.1590	2.5384± 0.1316	2.1896± 0.1130	2.7260± 0.1561

Table 4.12 Friction constant of polystyrene M = 600000 in cyclohexane.

Temperature (°C)	$\zeta_{01} \times 10^{10} \text{ kg.s}$	$-k_{\text{f}} \times 10^2 \text{ m}^3 \text{ kg}^{-1}$	$A_{21} \times 10^6 \text{ mol.m}^3 \text{ kg}^{-2}$
37.2	1.4495±0.0134	3.3002±0.1449	0.9297±0.0068
39.2	1.4015±0.0172	3.1339±0.1926	1.0492±0.0123
42.4	1.3469±0.0116	3.0197±0.1344	1.3333±0.0086
44.7	1.3119±0.0038	3.0120±0.1102	1.5584±0.0112
47.2	1.2791±0.0141	3.0637±0.1729	1.7999±0.0383
49.8	1.2416±0.0199	2.9984±0.2515	1.9417±0.0665

Table 4.13 Friction constant at zero concentration, constant  $k_{\text{f}}$ , and second virial coefficient A<sub>2</sub> for polystyrene M = 100000.

Temperature (°C)	$\zeta_0 \times 10^{10}$ kg.s	$-k_s \times 10^2$ m <sup>2</sup> .kg <sup>-1</sup>	$A_{22} \times 10^7$ mol.m <sup>3</sup> .kg <sup>-2</sup>
37.2	4.0856±0.0772	1.8503±0.0149	5.9431±0.1057
39.2	3.7626±0.0583	1.6814±0.0122	5.7546±0.1362
42.4	3.4109±0.0342	1.5472±0.0079	6.0597±0.0984
44.7	3.1986±0.0456	1.4421±0.0112	6.1609±0.1347
47.2	2.9976±0.0302	1.3929±0.0079	6.2775±0.0751
49.8	2.7763±0.0464	1.2150±0.0130	5.7509±0.1611

Table 4.14 Friction constant at zero concentration, constant  $k_s$ , and second virial coefficient  $A_2$  of polystyrene  $M = 600000$ .

Temperature (°C)	$\bar{D} = \frac{c_1 M_1 D_1 + c_2 M_2 D_2}{c_1 M_1 + c_2 M_2} \times 10^{11}$ m <sup>2</sup> .s <sup>-1</sup>				
	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
37.2	2.34988± 0.39714	2.01303± 0.32207	2.78216± 0.45693	1.73319± 0.28129	3.57559± 0.51593
39.2	2.44139± 0.37672	2.10268± 0.31860	2.89193± 0.42641	1.81759± 0.23185	3.67966± 0.51328
42.4	2.56353± 0.33745	2.24887± 0.34626	3.03882± 0.40652	1.93450± 0.30514	3.83321± 0.46269
44.7	2.69093± 0.27456	2.34438± 0.40783	3.14599± 0.39121	2.04900± 0.23056	3.95213± 0.54725
47.2	2.85153± 0.33784	2.45321± 0.28185	3.27090± 0.40345	2.13584± 0.29537	4.08908± 0.47256
49.8	3.01435± 0.39282	2.57051± 0.34599	3.39450± 0.39439	2.25035± 0.27433	4.21252± 0.56433

Table 4.15 Apparent diffusion coefficient of samples 3 – 7.

Temperature (°C)	$M = 100000$		$M = 600000$	
	$k_D \times 10^2 \text{ m}^3 \text{kg}^{-1}$	$k_\zeta \times 10^2 \text{ m}^3 \text{kg}^{-1}$	$k_D \times 10 \text{ m}^3 \text{kg}^{-1}$	$k_\zeta \times 10 \text{ m}^3 \text{kg}^{-1}$
37.2	$5.0186 \pm 0.5886$	$8.8326 \pm 1.0339$	$1.9517 \pm 0.1491$	$3.3876 \pm 0.2516$
39.2	$5.6758 \pm 0.9496$	$9.9677 \pm 0.1664$	$1.8895 \pm 0.1980$	$3.2801 \pm 0.3348$
42.4	$7.2382 \pm 0.5248$	$12.6665 \pm 0.9147$	$1.9902 \pm 0.1362$	$3.4540 \pm 0.2297$
44.7	$8.4760 \pm 0.5851$	$14.8045 \pm 1.0163$	$2.0236 \pm 0.1836$	$3.5117 \pm 0.3092$
47.2	$9.8044 \pm 1.7367$	$17.0989 \pm 3.0070$	$2.0621 \pm 0.1006$	$3.5782 \pm 0.1692$
49.8	$10.5842 \pm 2.8027$	$18.4458 \pm 4.4843$	$1.8883 \pm 0.2343$	$3.2780 \pm 0.3962$

Table 4.16 Constants  $k_D$  and  $k_\zeta$ , which are evaluated from theory.

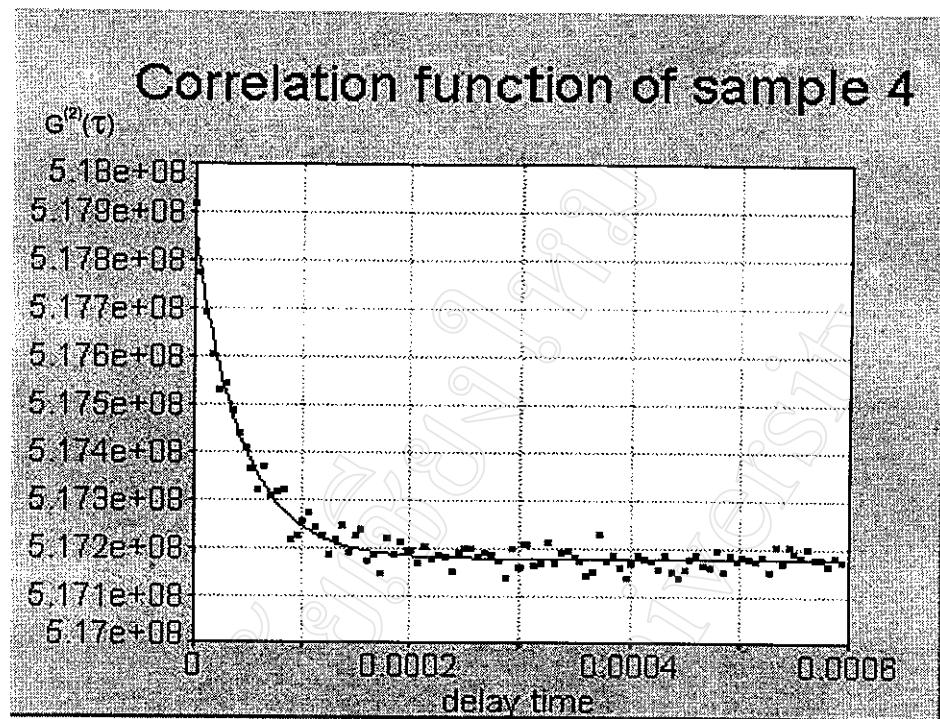


Figure 4.3 The photon correlation function versus delay time from the sample 4,  $M=100000$  with  $c_1=3.5$  mg/ml and  $M=600000$  with  $c_2=1.3$  mg/ml, at the temperature  $49.8^\circ\text{C}$ , taken with 4500 run.

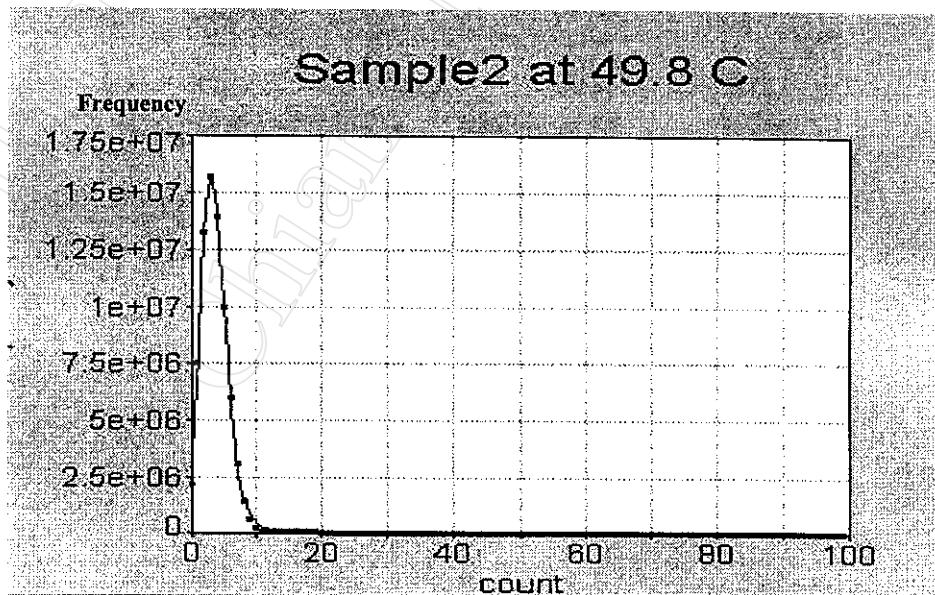


Figure 4.4 Distribution of photon count of scattering intensity from sample 2, polystyrene  $M = 600000$  and concentration is 2 mg/ml, taken with 4500 runs.

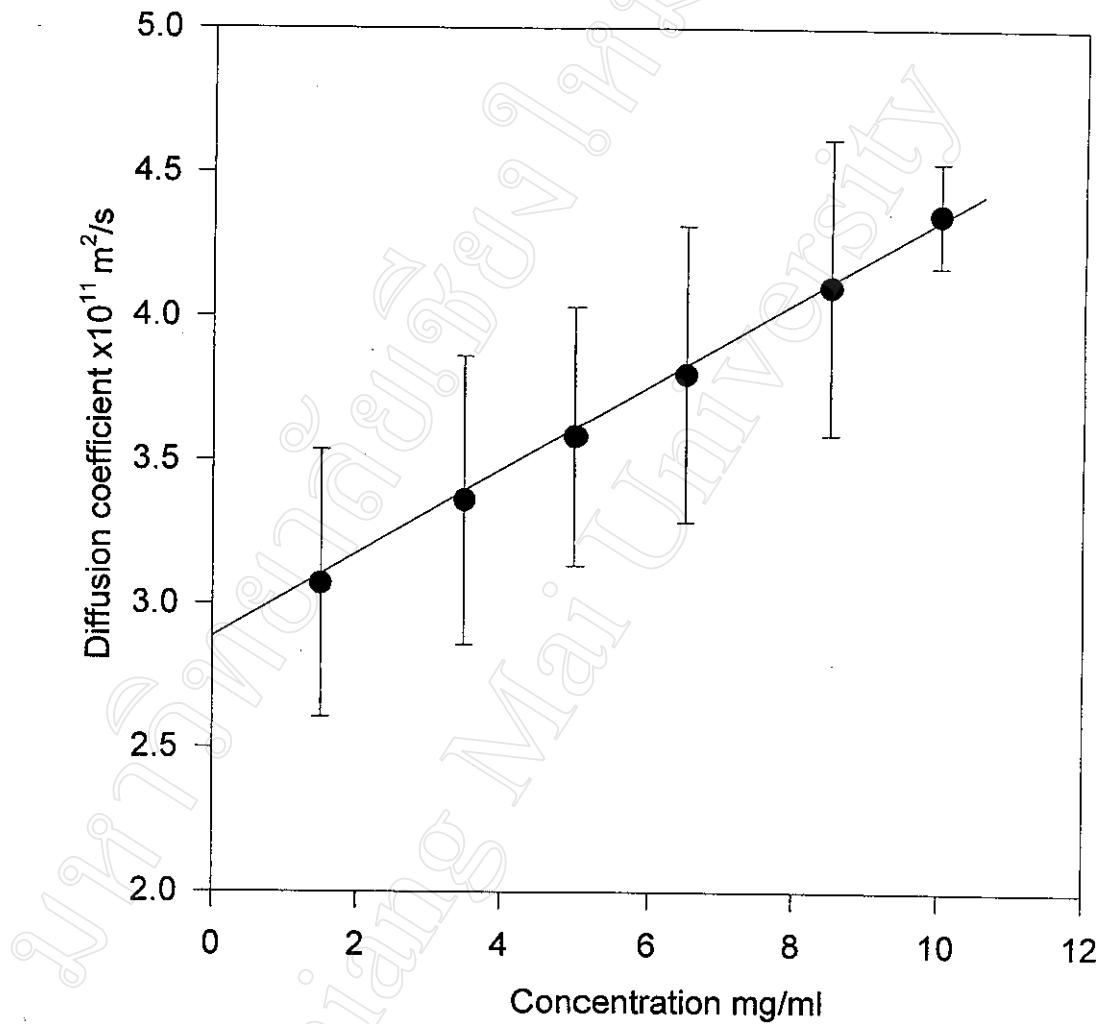


Figure 4.5 Plot of diffusion coefficient versus concentration of polystyrene

$M = 100000$  in cyclohexane at temperature  $37.2 \text{ } ^\circ\text{C}$

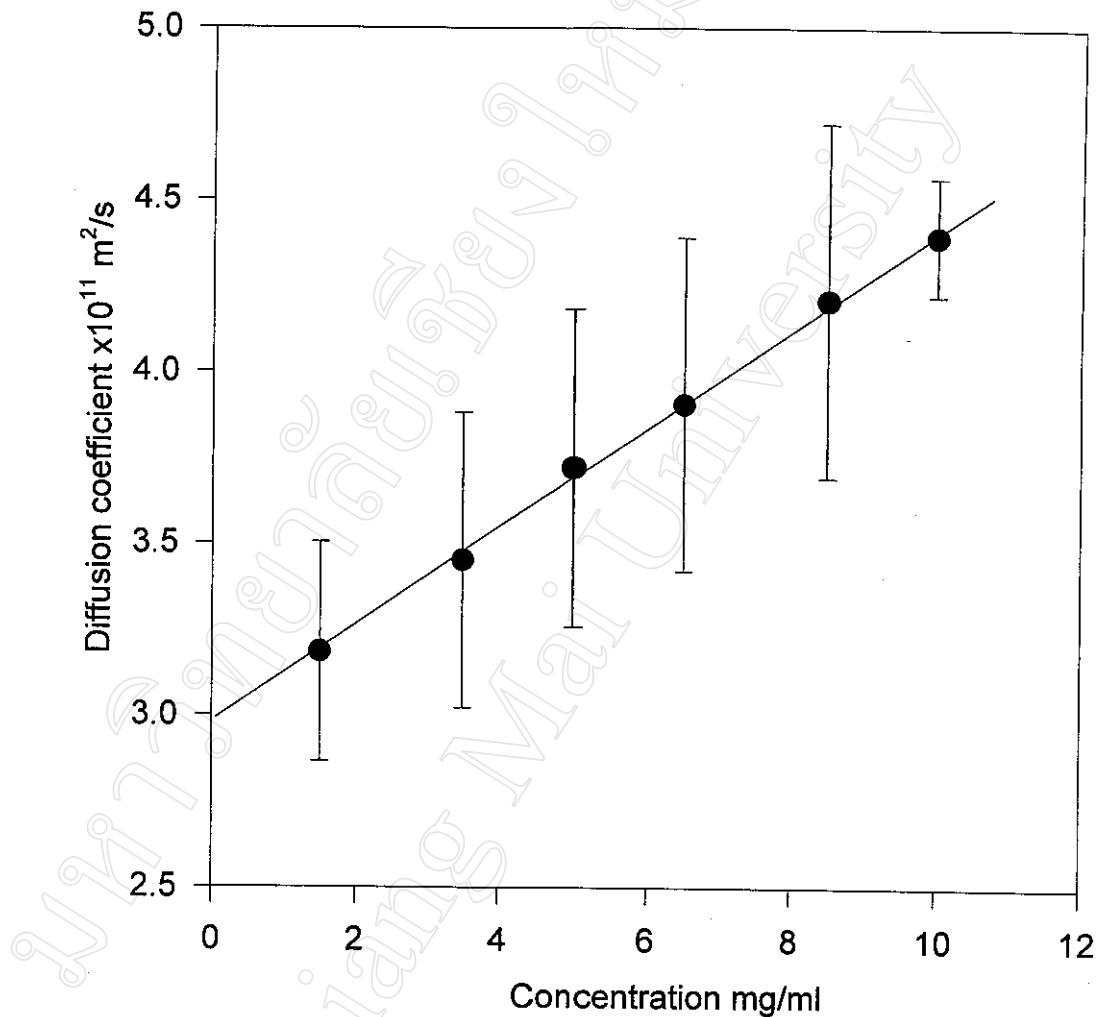


Figure 4.6 Plot of diffusion coefficient versus concentration of polystyrene  
M = 100000 in cyclohexane at temperature 39.2 °C

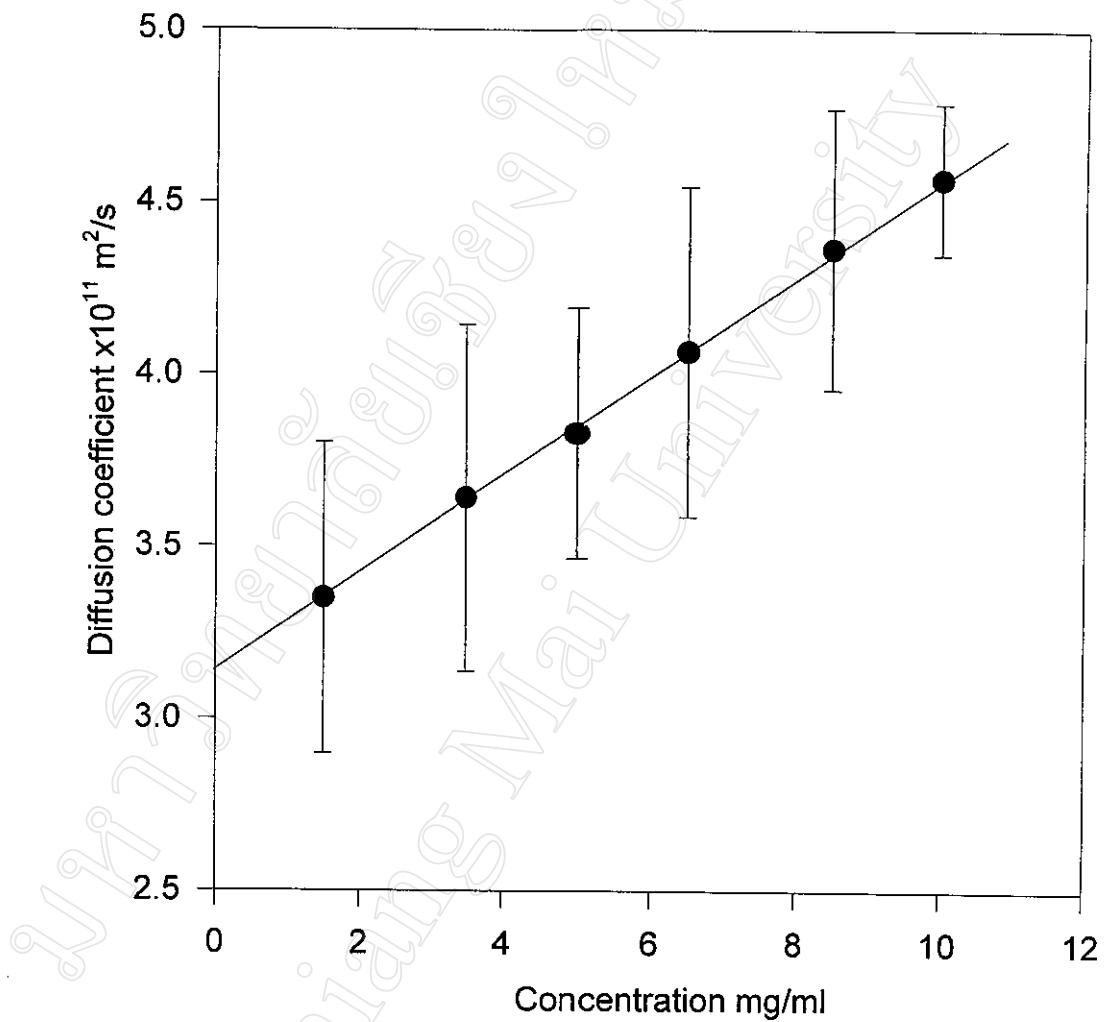


Figure 4.7 Plot of diffusion coefficient versus concentration of polystyrene  
M = 100000 in cyclohexane at temperature 42.4 °C

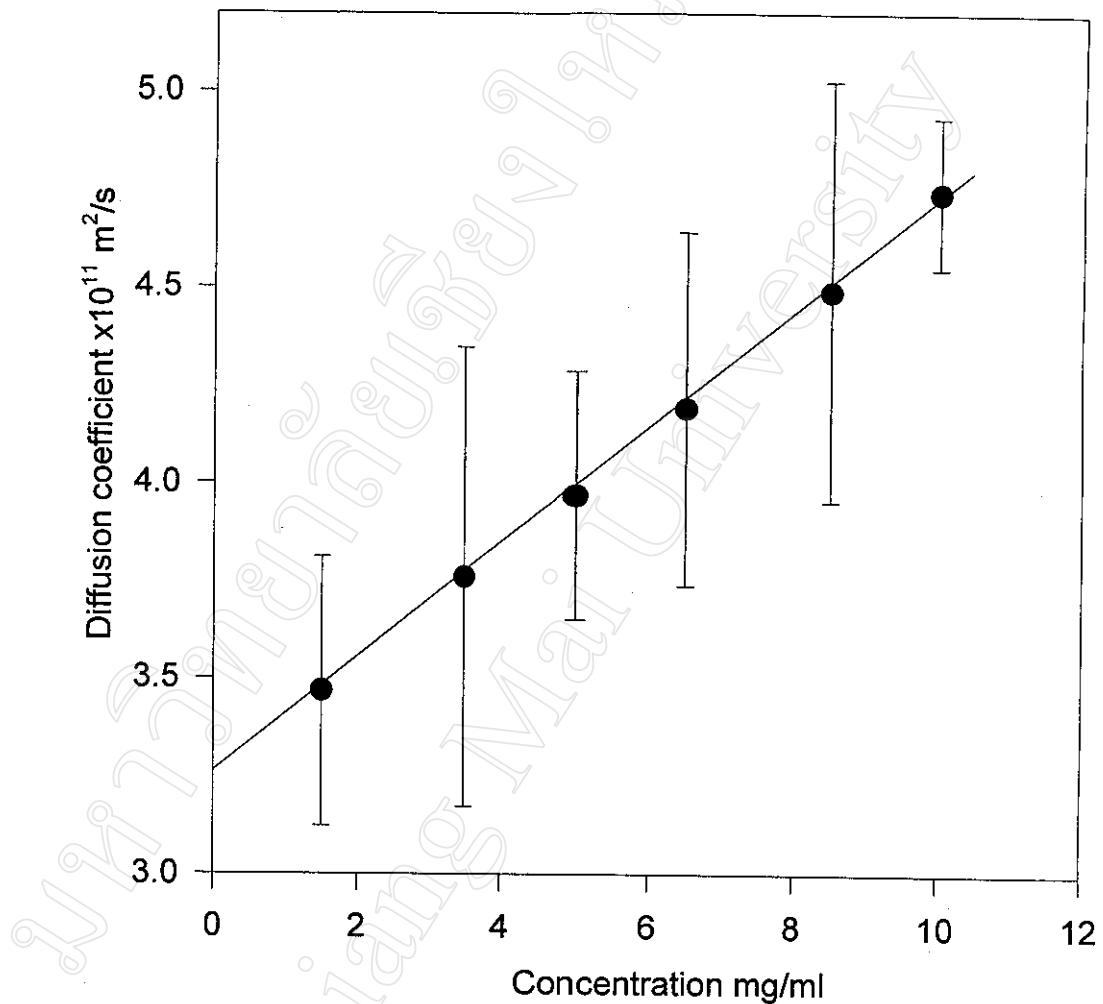


Figure 4.8 Plot of diffusion coefficient versus concentration of polystyrene  
M = 100000 in cyclohexane at temperature 44.7 °C

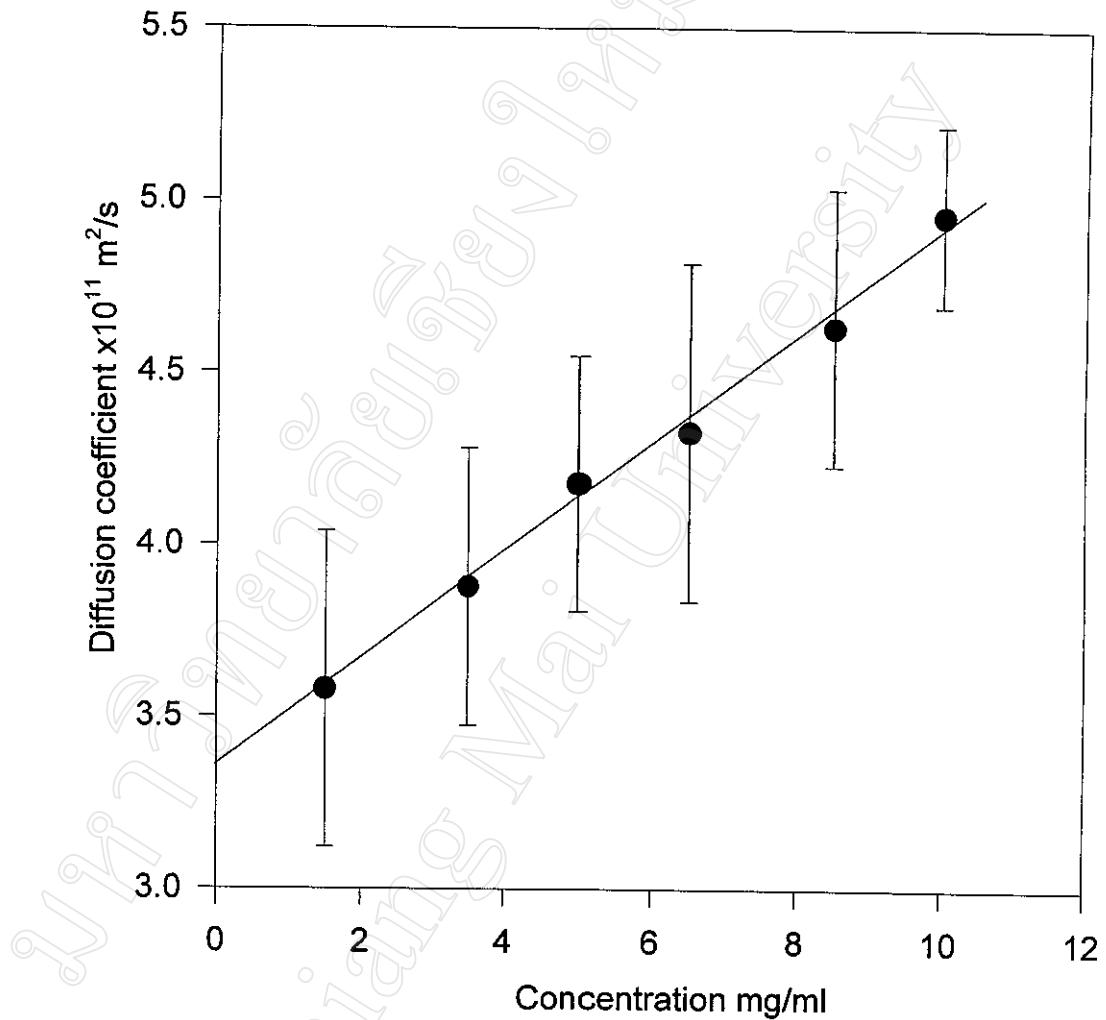


Figure 4.9 Plot of diffusion coefficient versus concentration of polystyrene  
M = 100000 in cyclohexane at temperature 47.2 °C

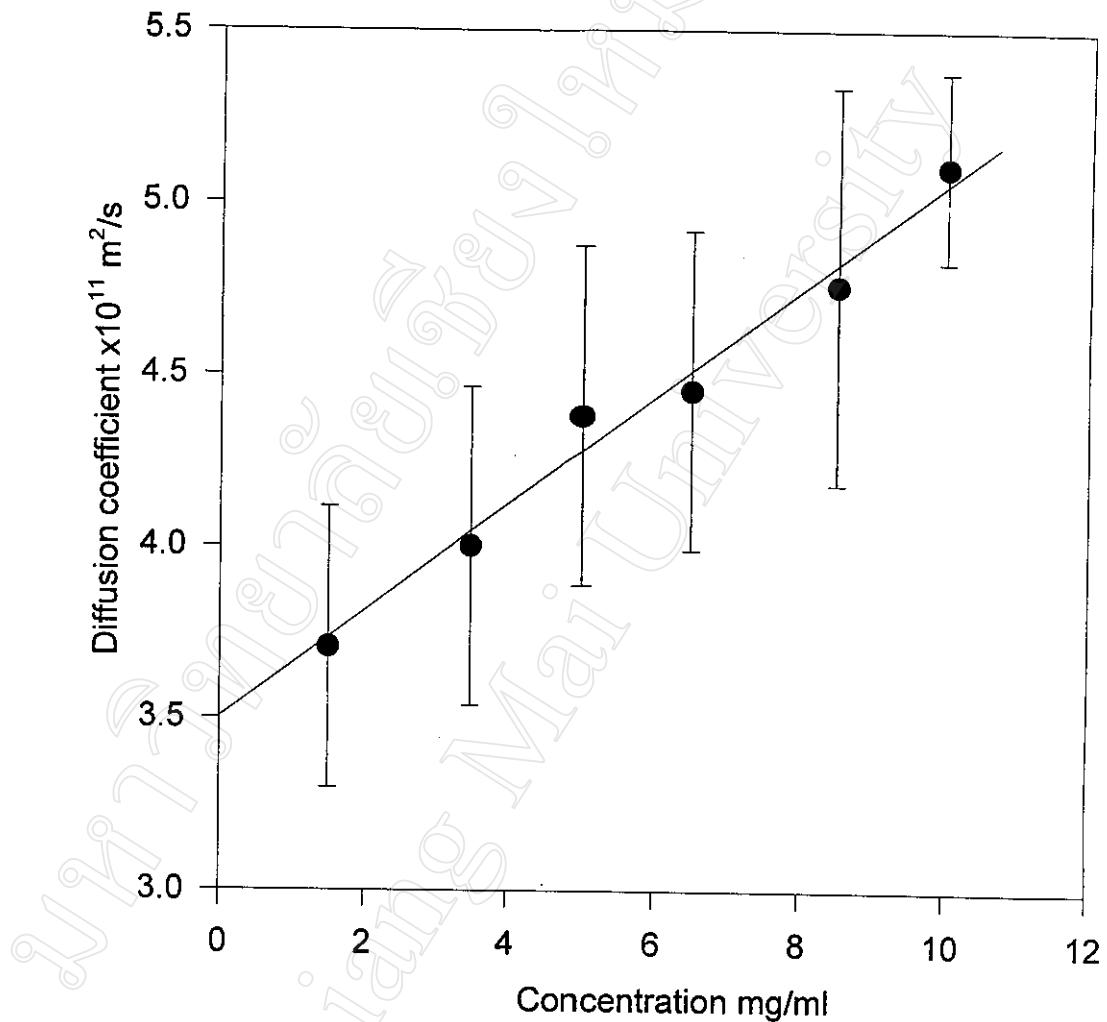


Figure 4.10 Plot of diffusion coefficient versus concentration of polystyrene  
M = 100000 in cyclohexane at temperature 49.8 °C

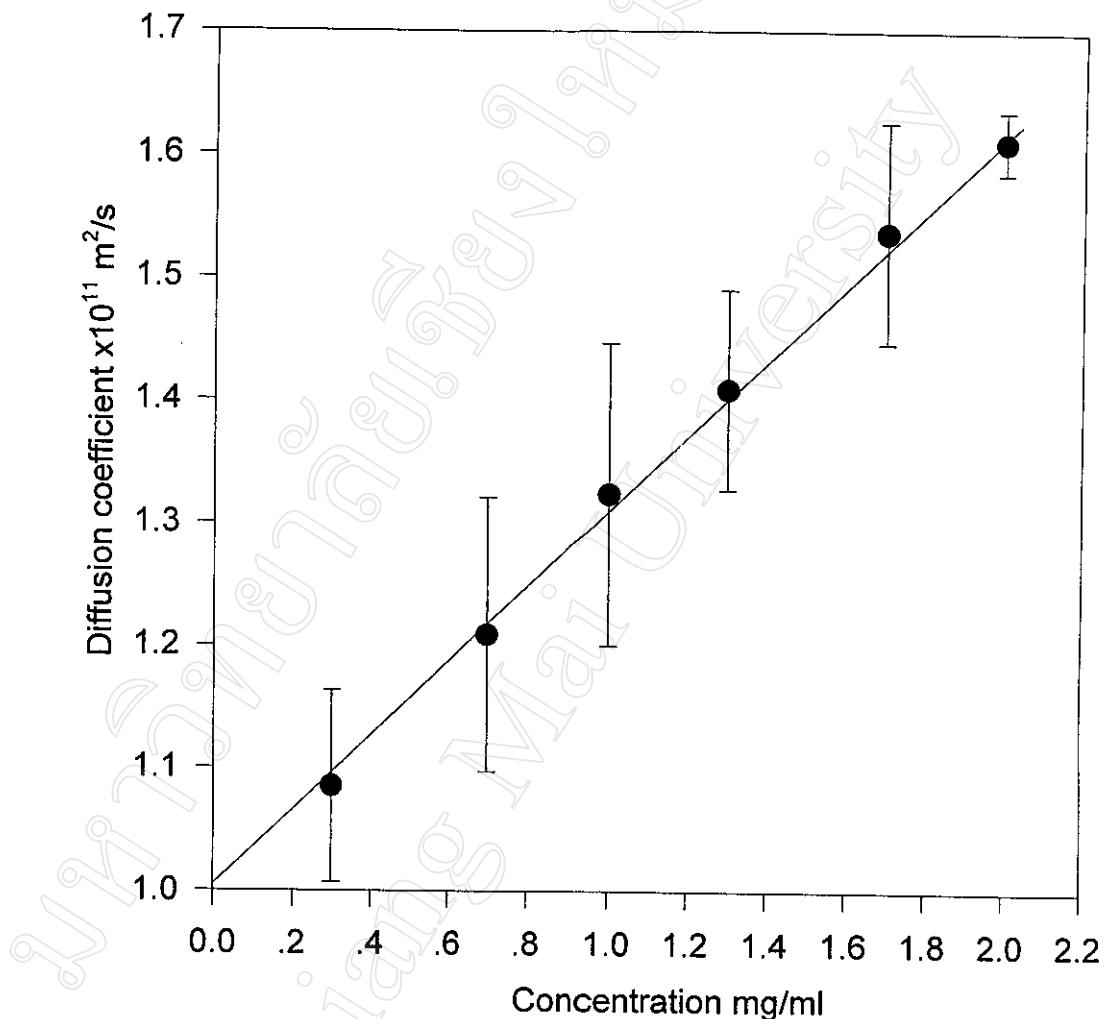


Figure 4.11 Plot of diffusion coefficient versus concentration of polystyrene  
M = 600000 in cyclohexane at temperature 37.2 °C

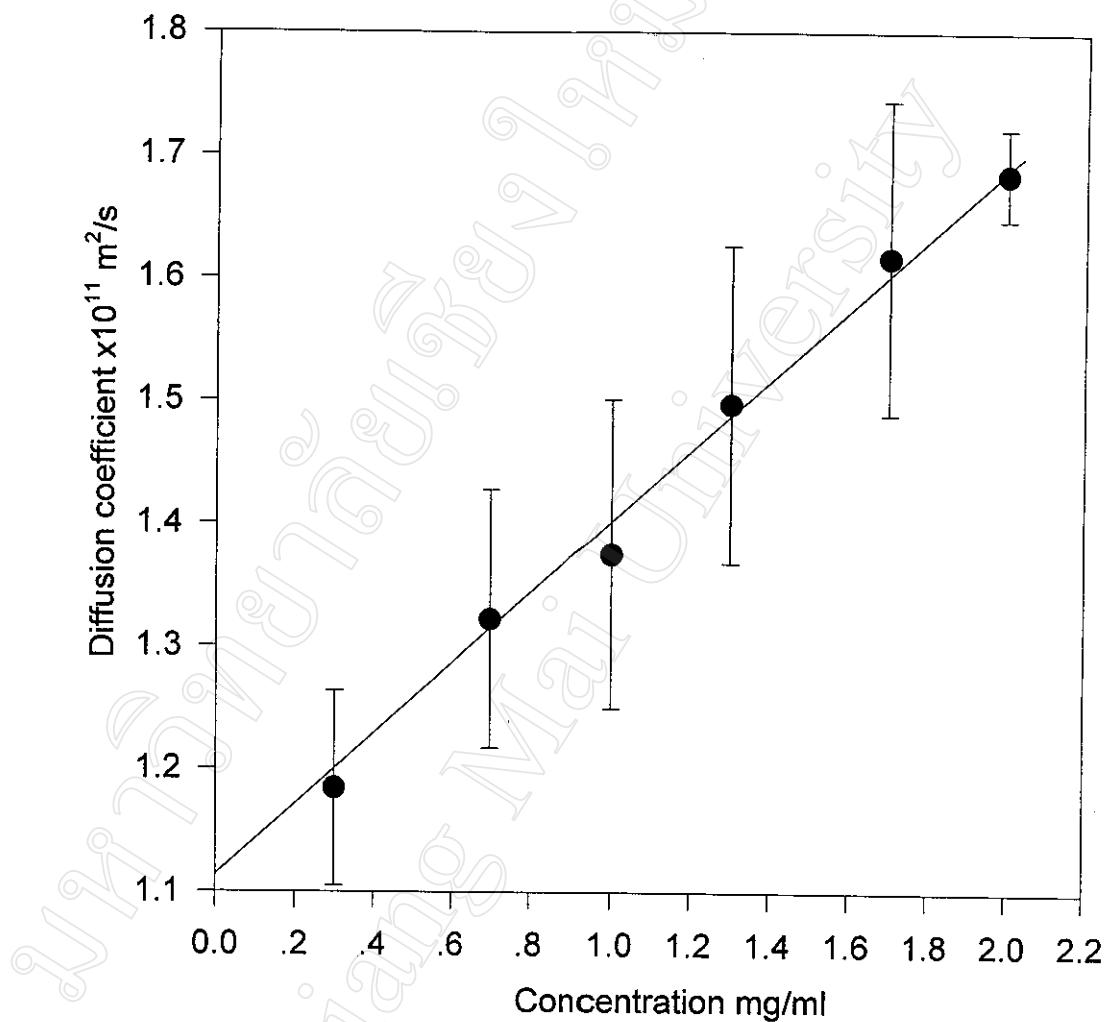


Figure 4.12 Plot of diffusion coefficient versus concentration of polystyrene  
M = 600000 in cyclohexane at temperature 39.2 °C

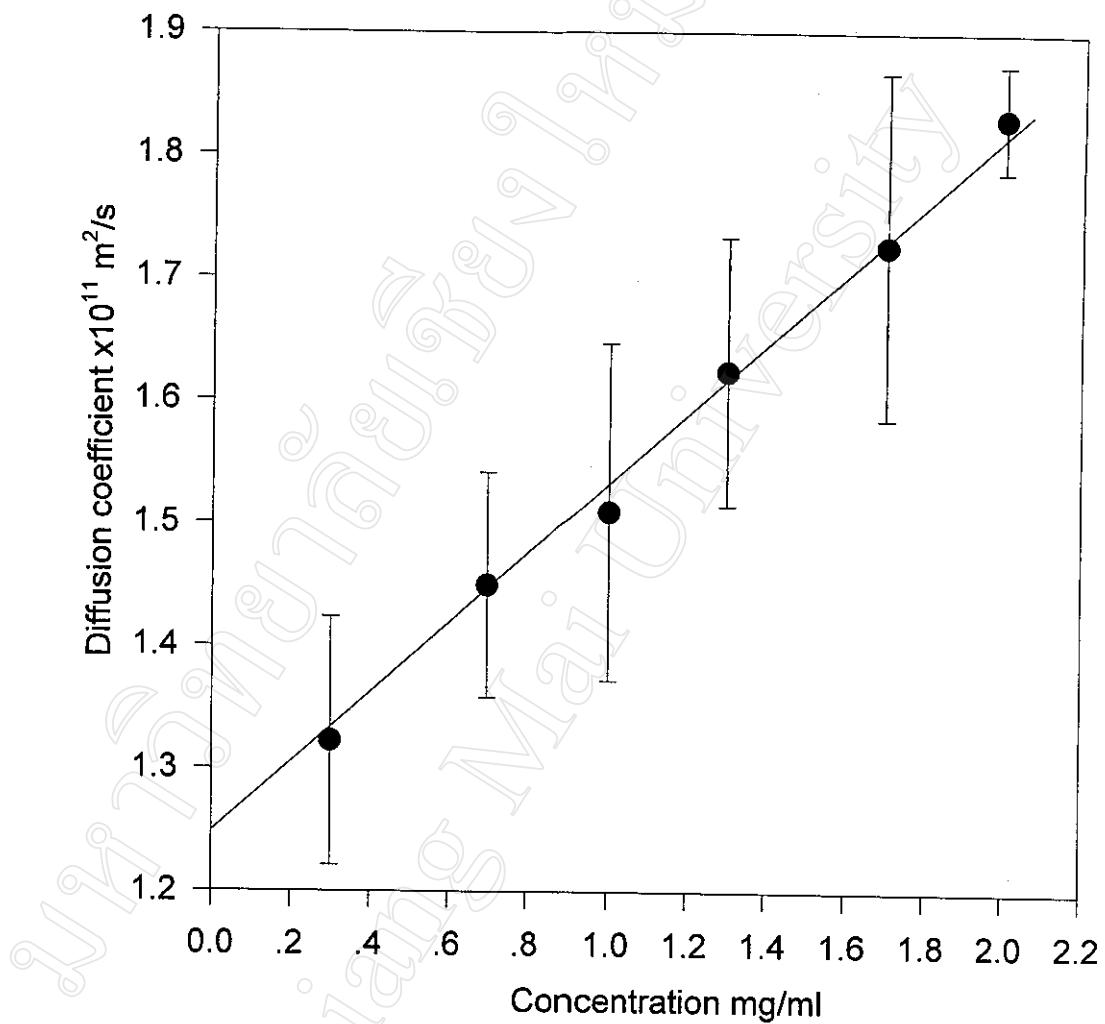


Figure 4.13 Plot of diffusion coefficient versus concentration of polystyrene  
M = 600000 in cyclohexane at temperature 42.4 °C

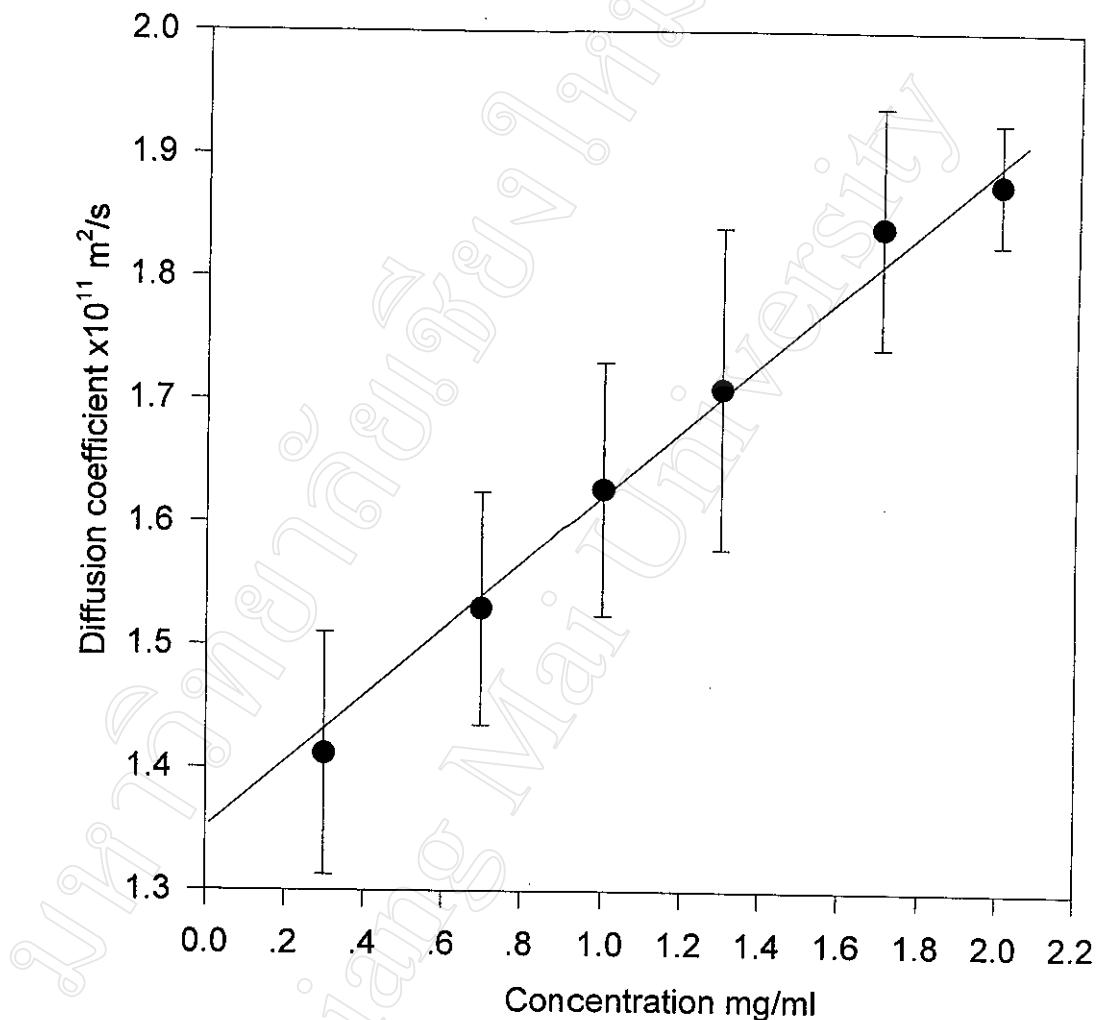


Figure 4.14 Plot of diffusion coefficient versus concentration of polystyrene  
M = 600000 in cyclohexane at temperature 44.7 °C

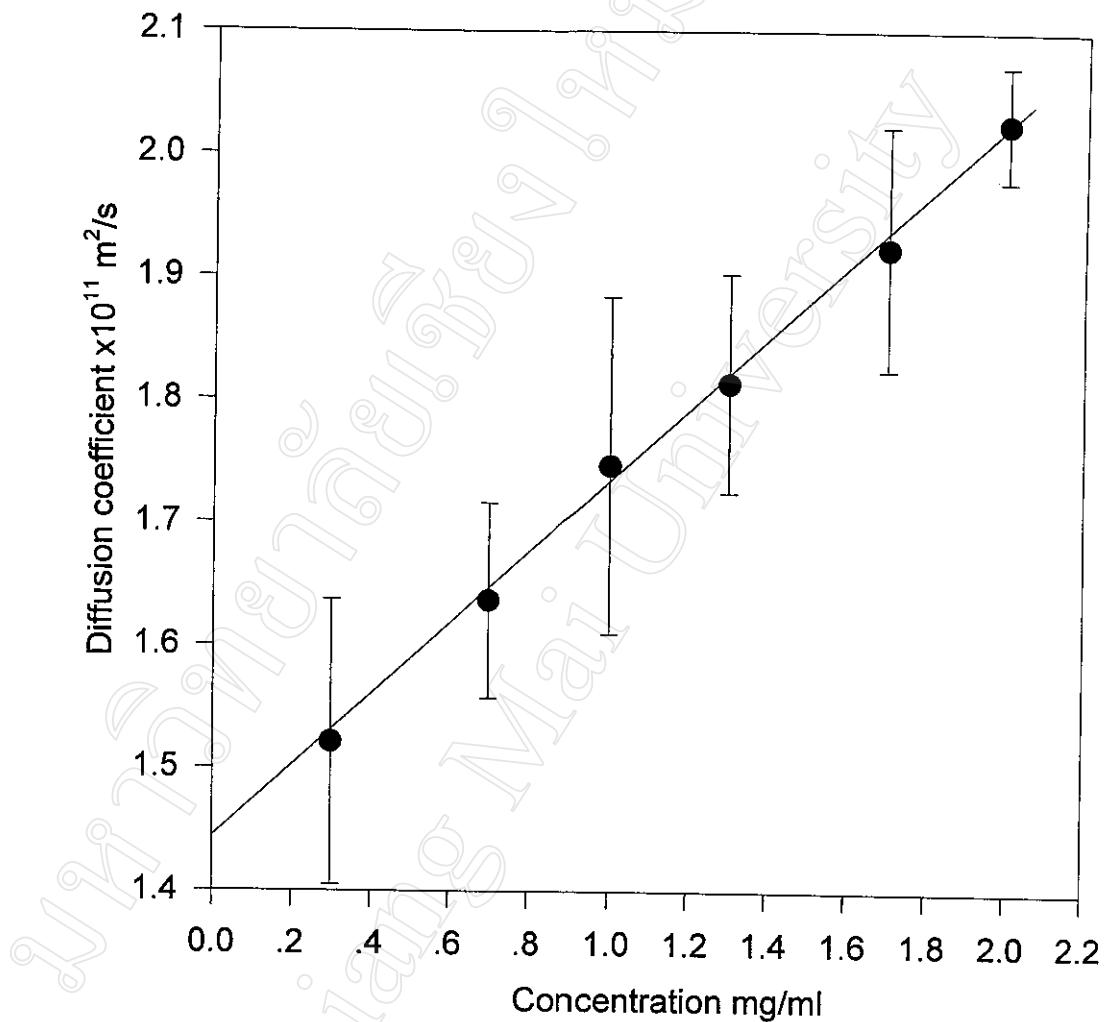


Figure 4.15 Plot of diffusion coefficient versus concentration of polystyrene  
M = 600000 in cyclohexane at temperature 47.2 °C

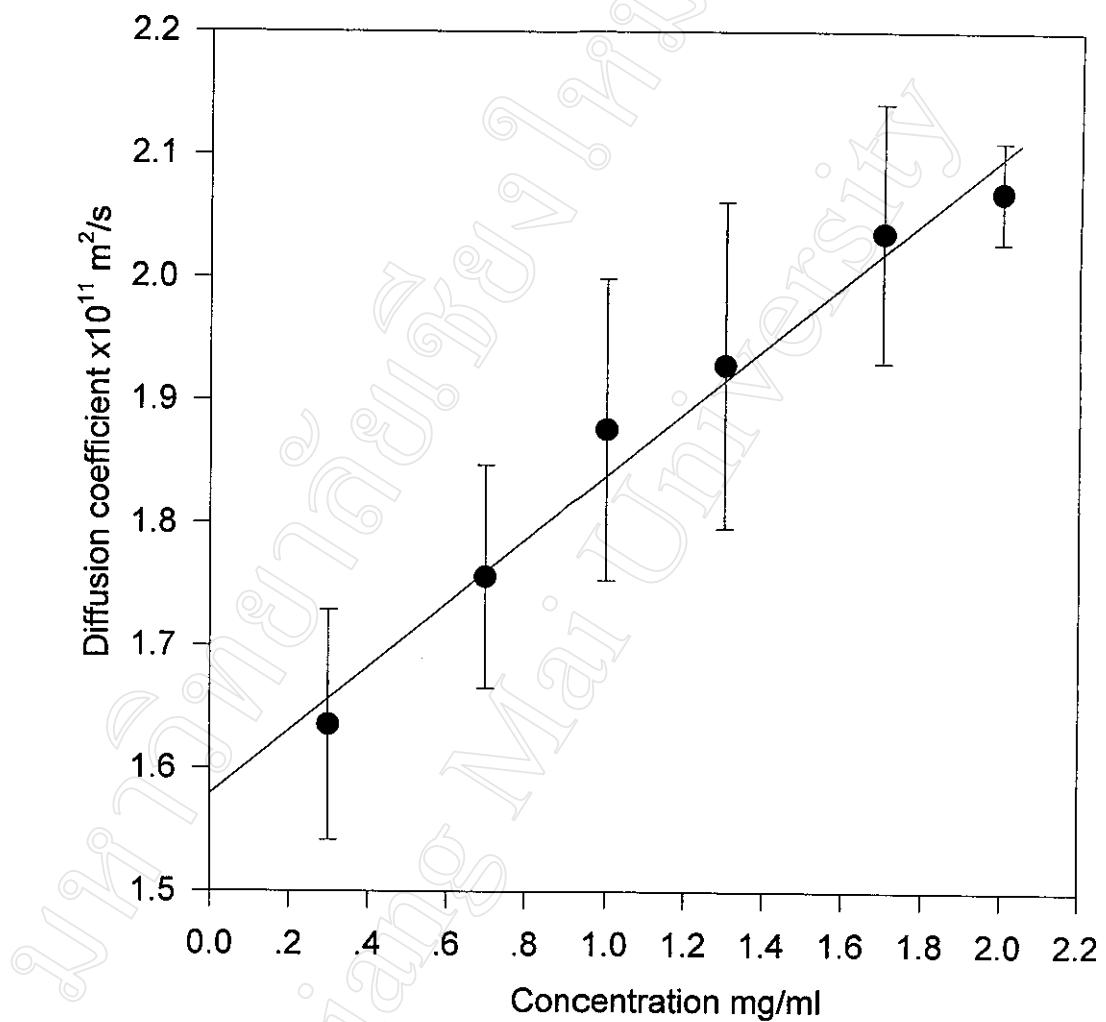


Figure 4.16 Plot of diffusion coefficient versus concentration of polystyrene  
M = 600000 in cyclohexane at temperature 49.8 °C

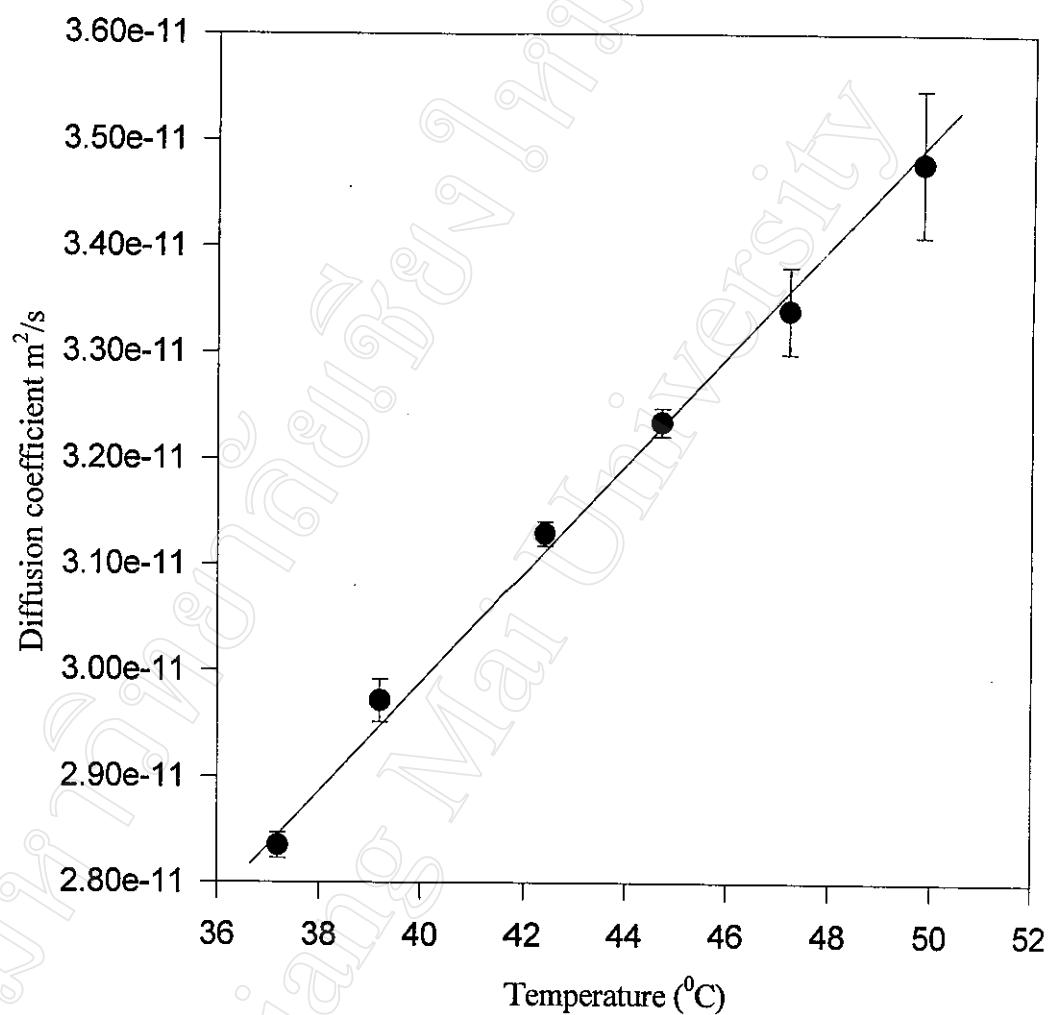


Figure 4.19 Plot of diffusion coefficient at zero concentration for polystyrene  
M = 100000 in cyclohexane versus temperature.

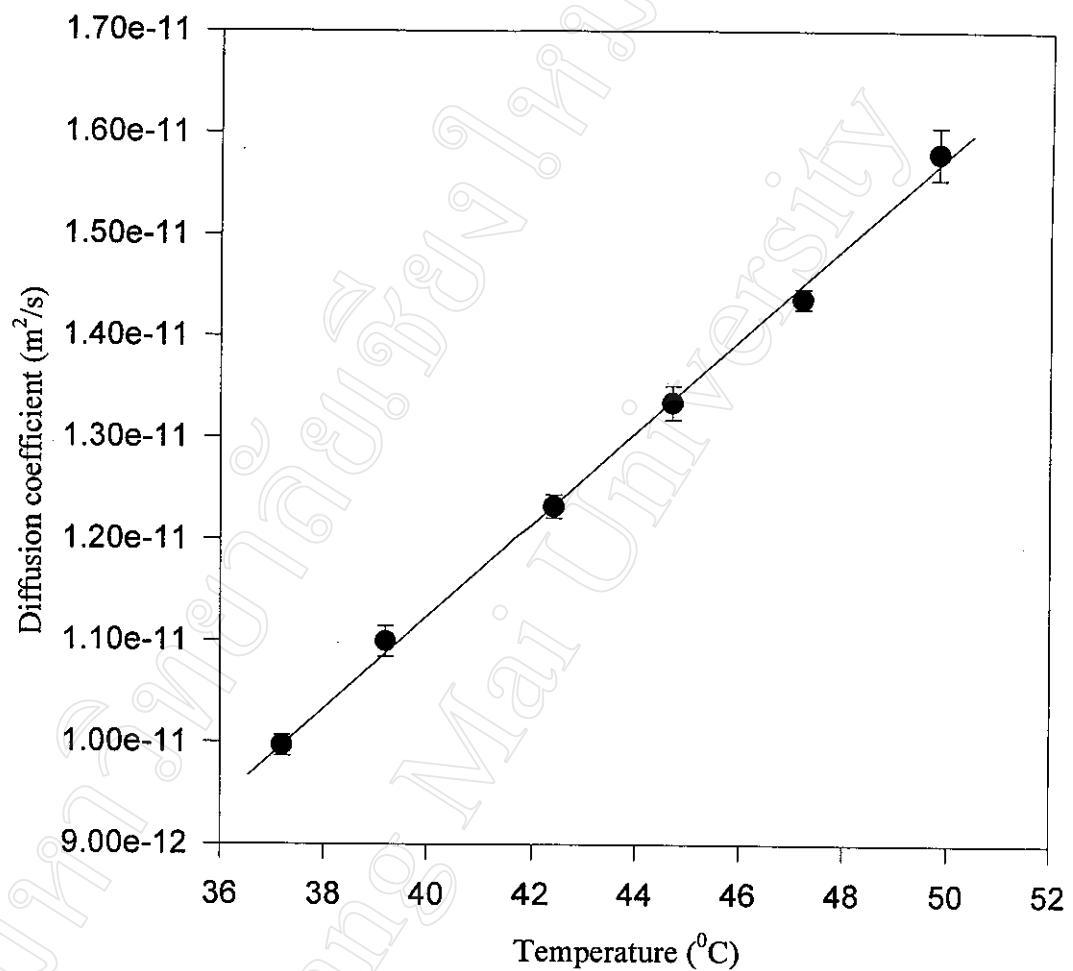


Figure 4.20 Plot of diffusion coefficient at zero concentration of polystyrene  
M=600000 in cyclohexane versus temperature.

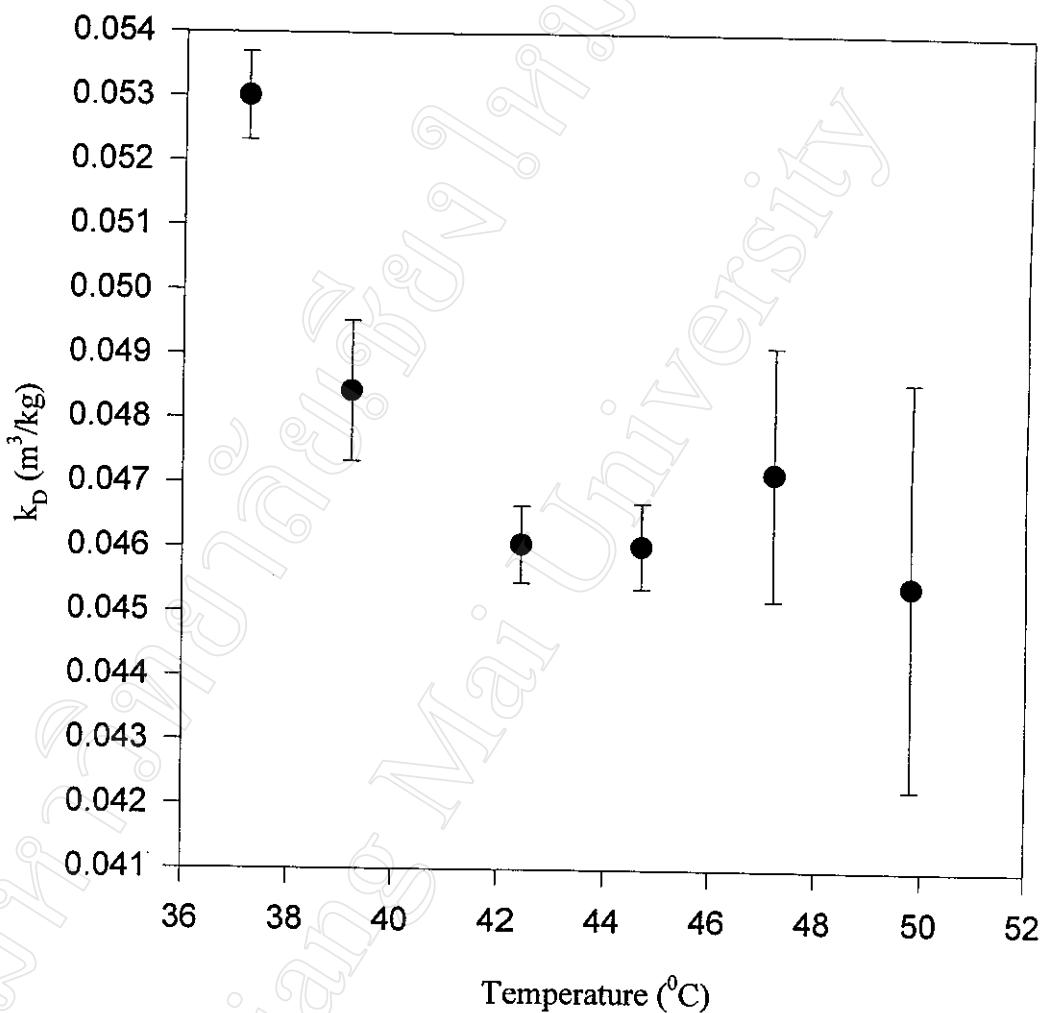


Figure 4.21 Plot of constant  $k_D$  of polystyrene  $M=100000$  in cyclohexane versus temperature.

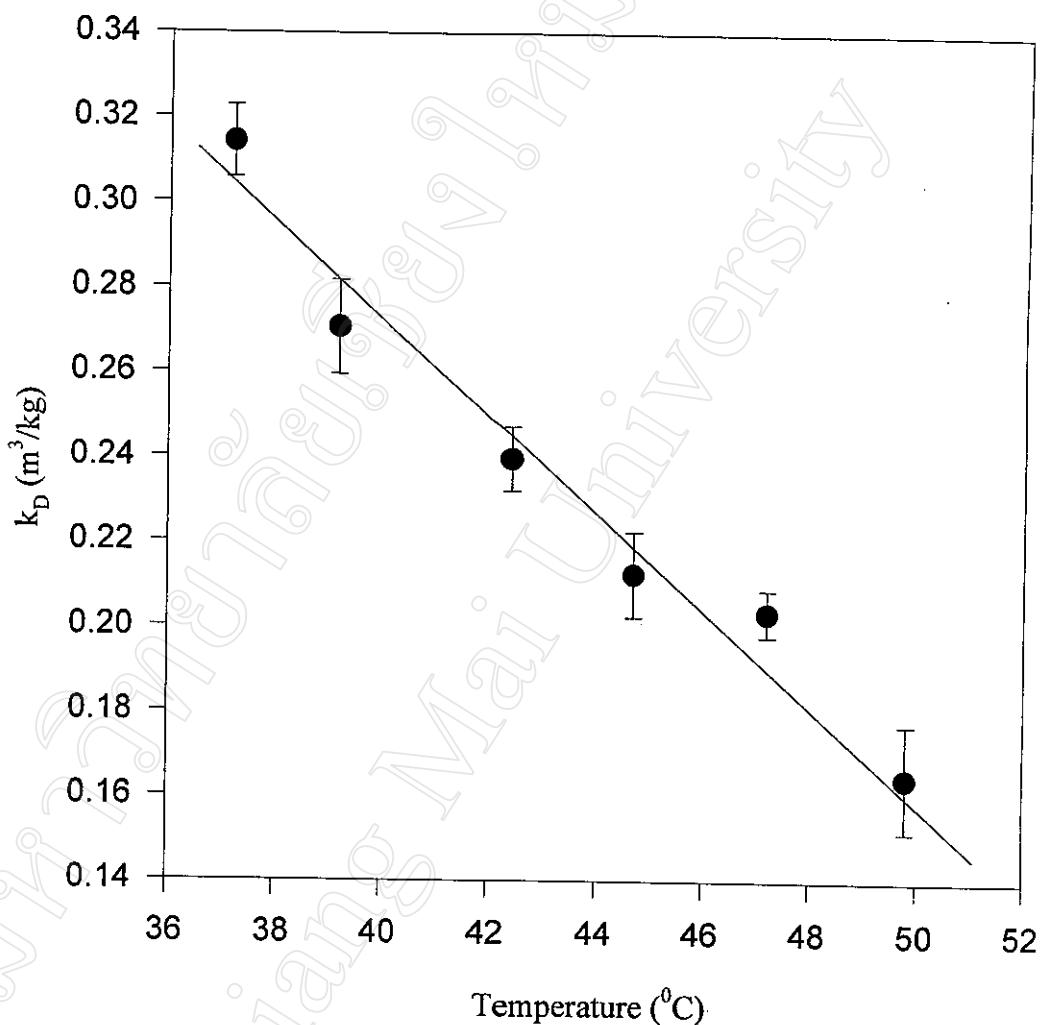


Figure 4.22 Plot of constant  $k_D$  of polystyrene  $M=600000$  in cyclohexane versus temperature.

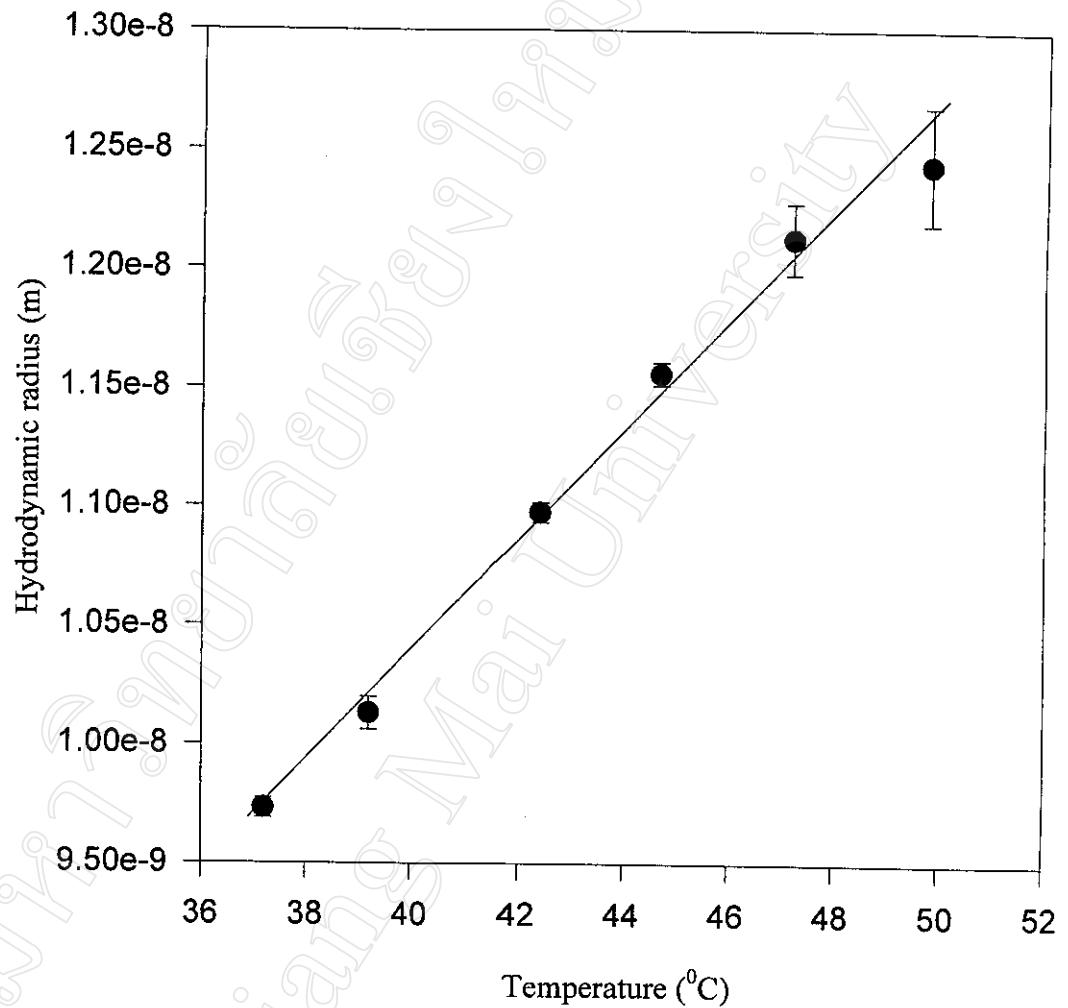


Figure 4.23 Plot of hydrodynamic radius of polystyrene M=100000 at zero concentration versus temperature.

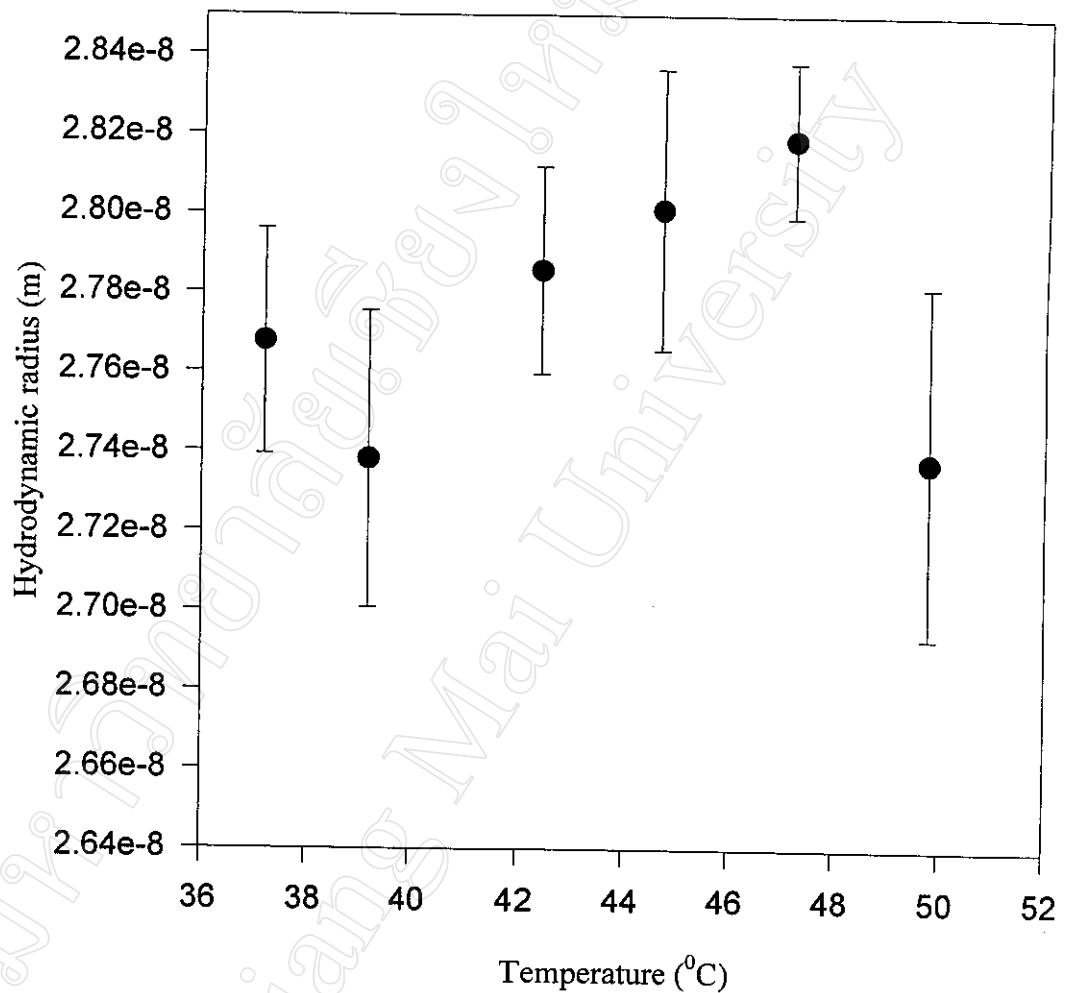


Figure 4.24 Plot of hydrodynamic radius of polystyrene M=600000 at zero concentration versus temperature.

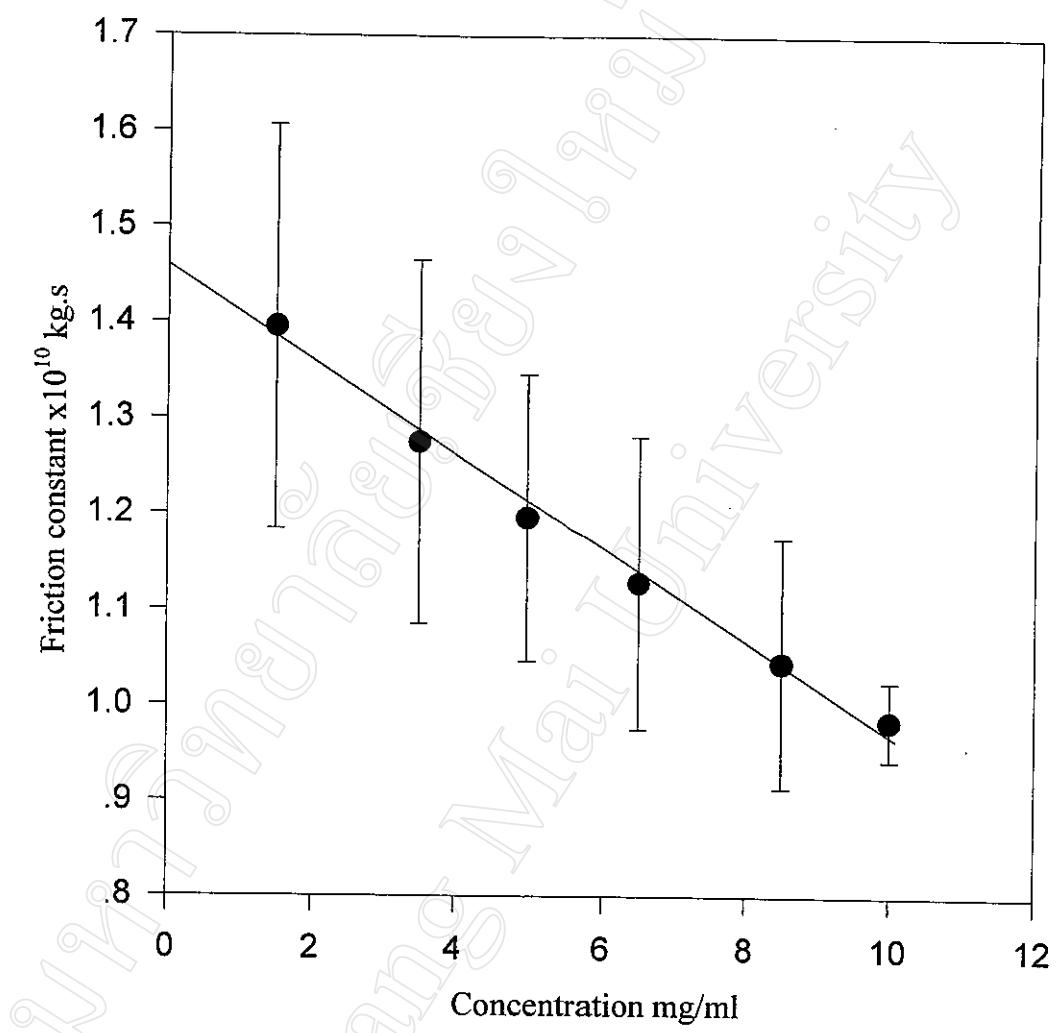


Figure 4.23 Plot of friction constant versus concentration of polystyrene  $M = 100000$  in cyclohexane at temperature  $37.2^\circ\text{C}$

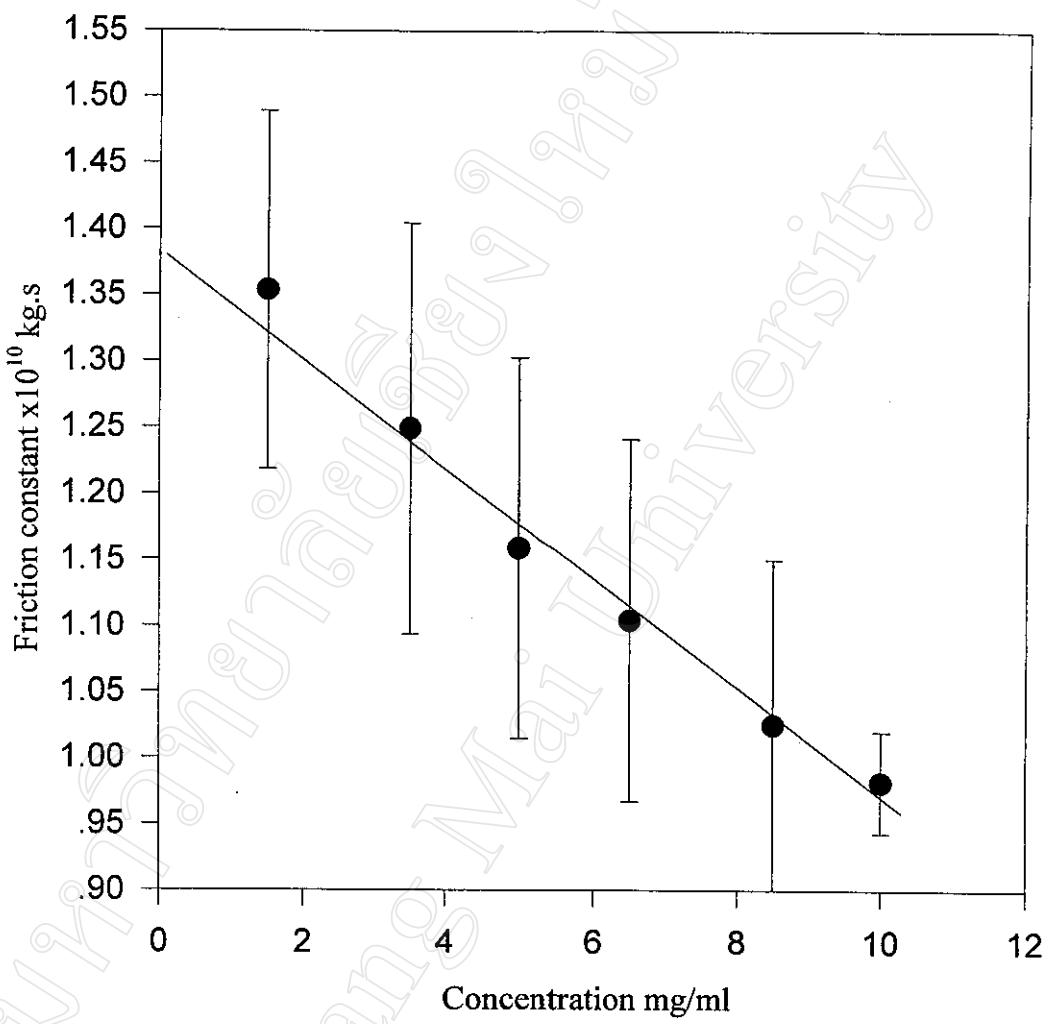


Figure 4.24 Plot of friction constant versus concentration of polystyrene  $M = 100000$  in cyclohexane at temperature  $39.2^\circ\text{C}$

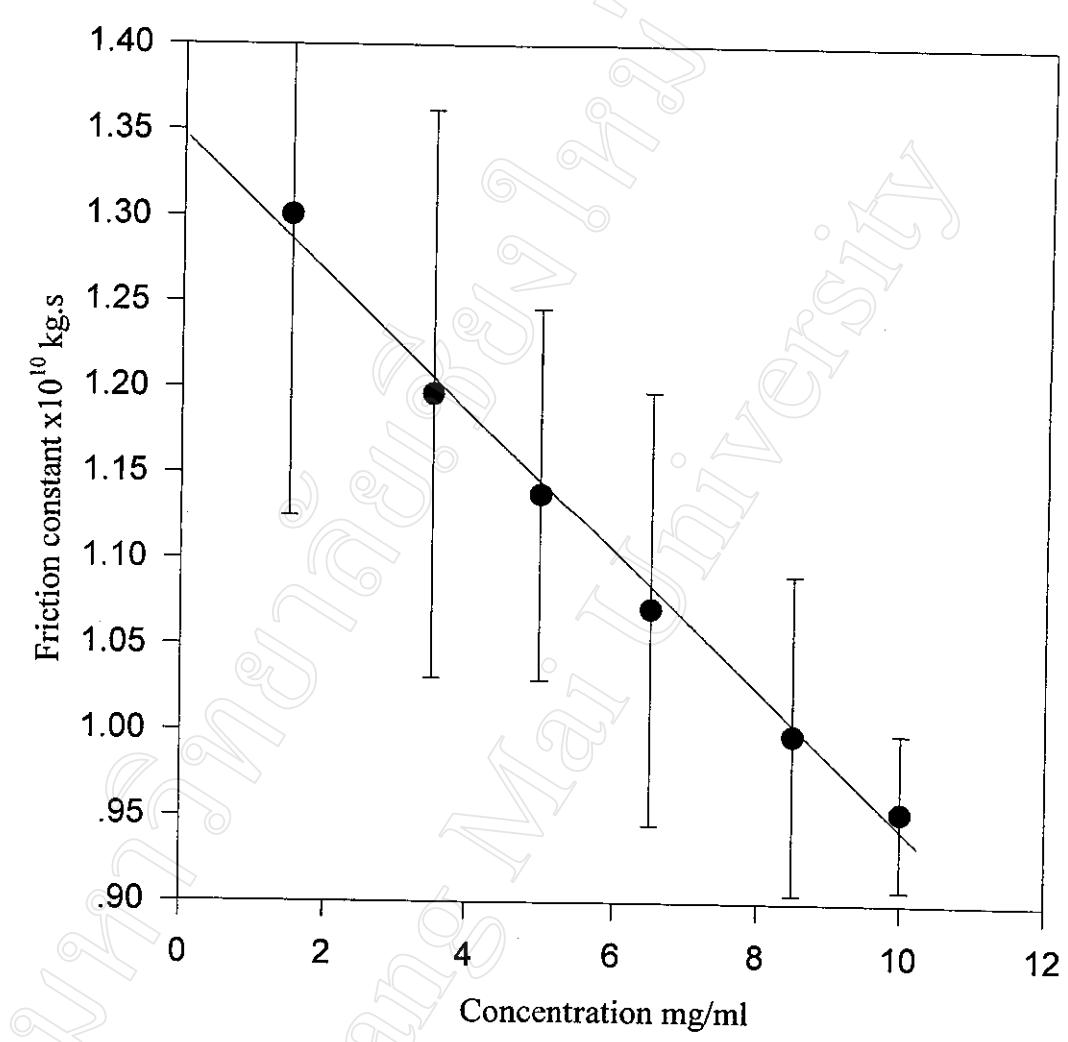


Figure 4.25 plot of friction constant versus concentration of polystyrene  $M = 100000$  in cyclohexane at temperature  $42.4^\circ\text{C}$

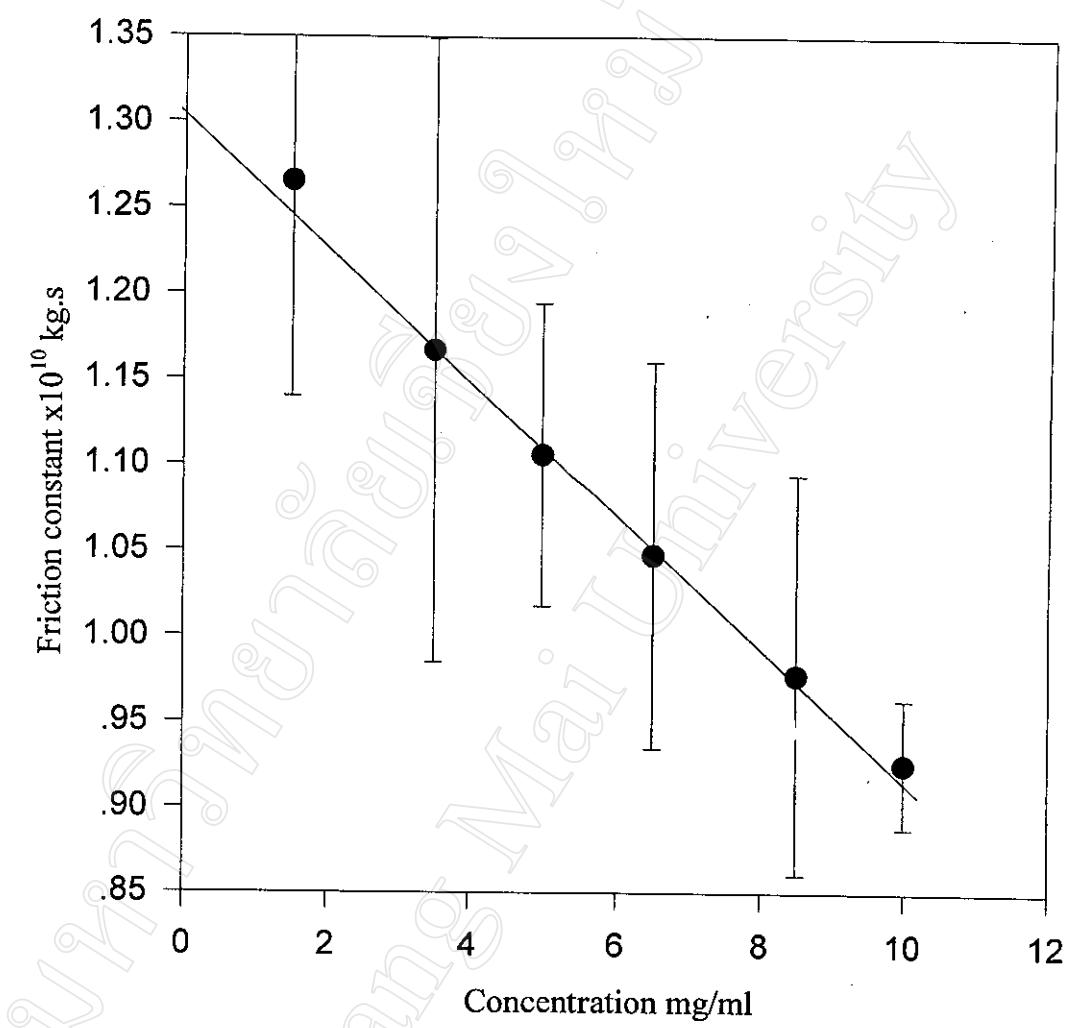


Figure 4.26 Plot of friction constant versus concentration of polystyrene  $M = 100000$  in cyclohexane at temperature  $44.7^\circ\text{C}$

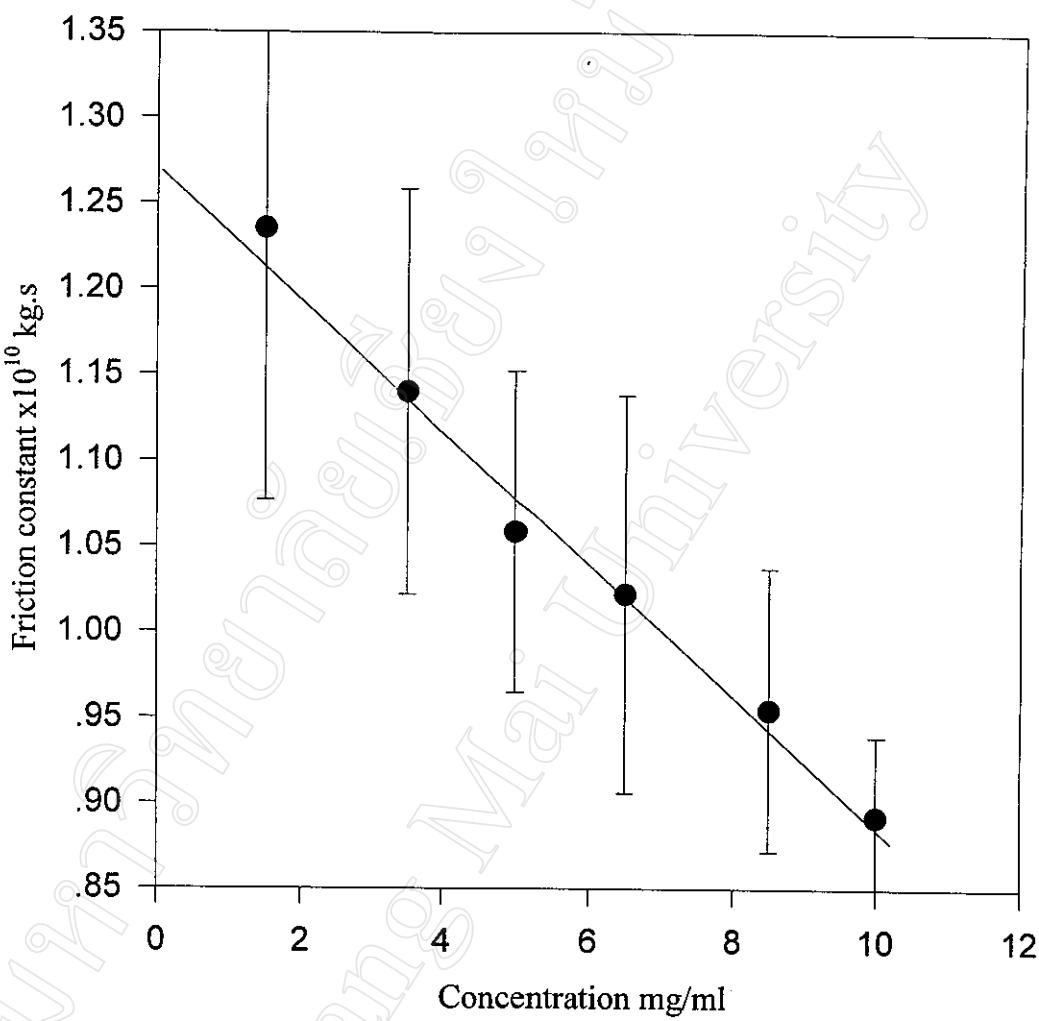


Figure 4.27 Plot of friction constant versus concentration of polystyrene  $M = 100000$  in cyclohexane at temperature  $47.2\text{ }^\circ\text{C}$

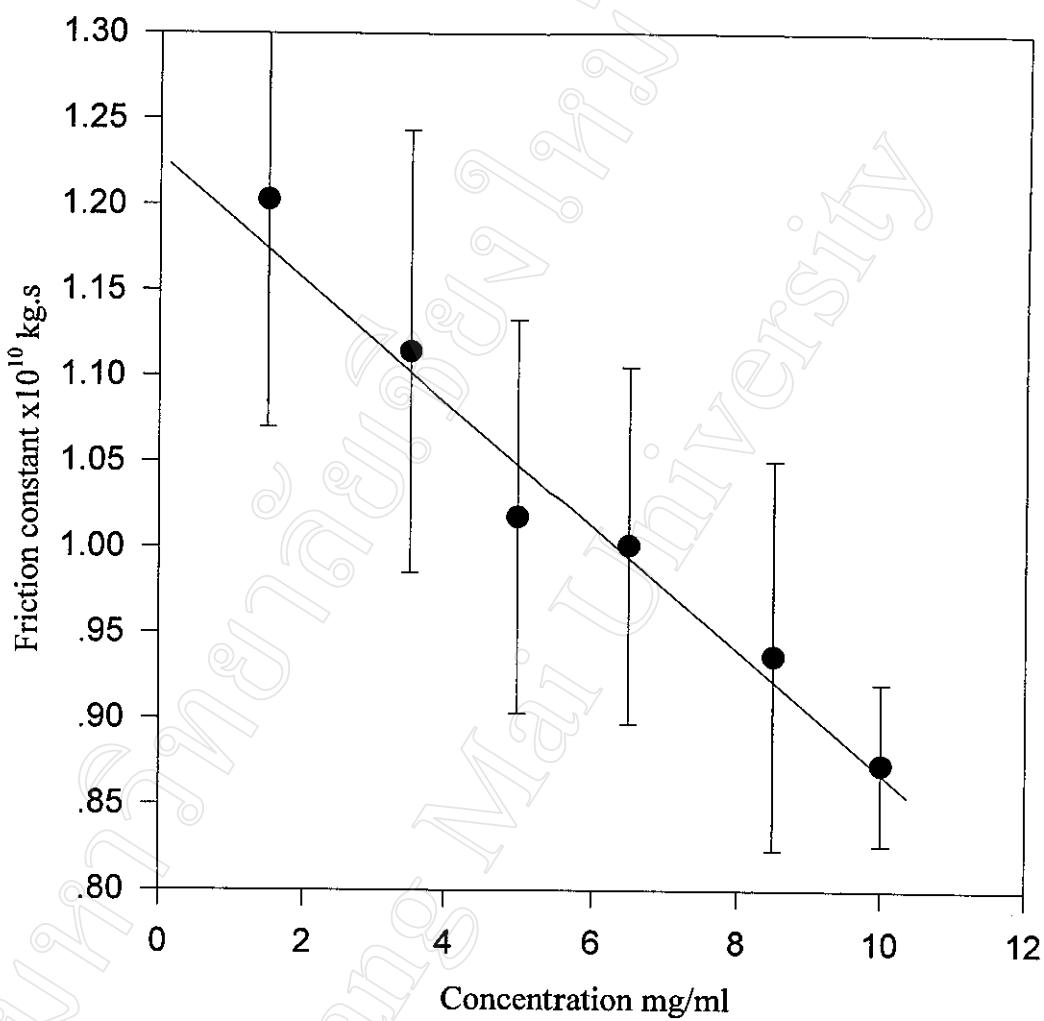


Figure 4.28 Plot of friction constant versus concentration of polystyrene  $M = 100000$  in cyclohexane at temperature  $49.8\text{ }^\circ\text{C}$

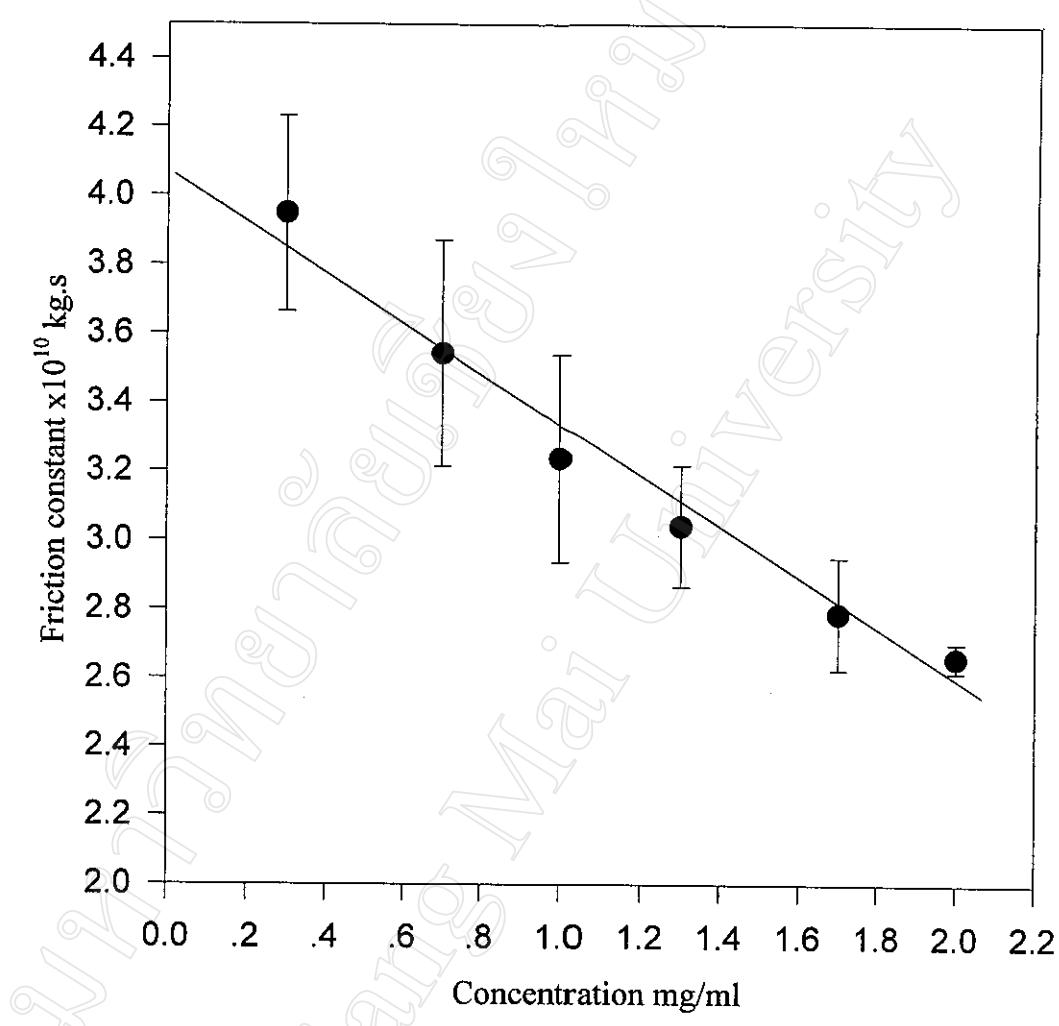


Figure 4.29 Plot of friction constant versus concentration of polystyrene  $M = 600000$  in cyclohexane at temperature  $37.2\text{ }^\circ\text{C}$

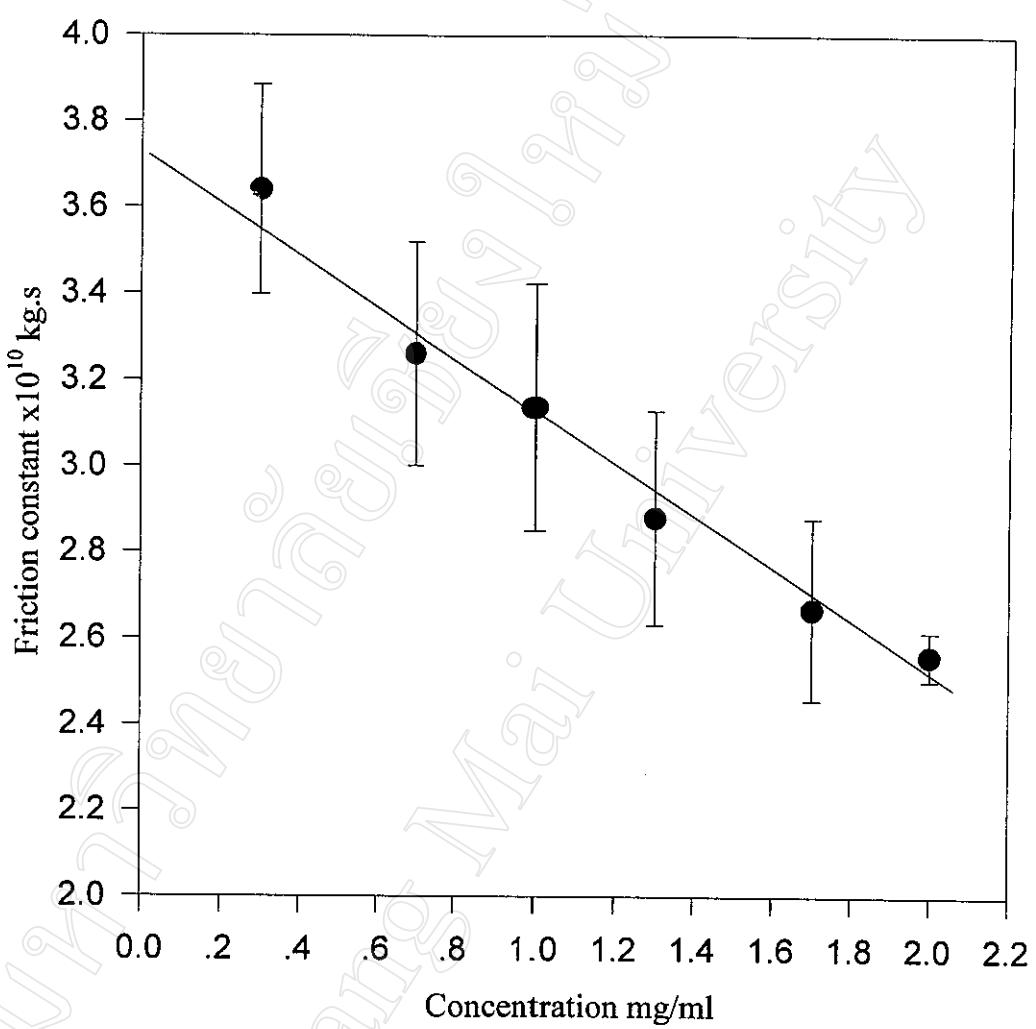


Figure 4.30 Plot of friction constant versus concentration of polystyrene  $M = 600000$  in cyclohexane at temperature  $39.2^\circ\text{C}$

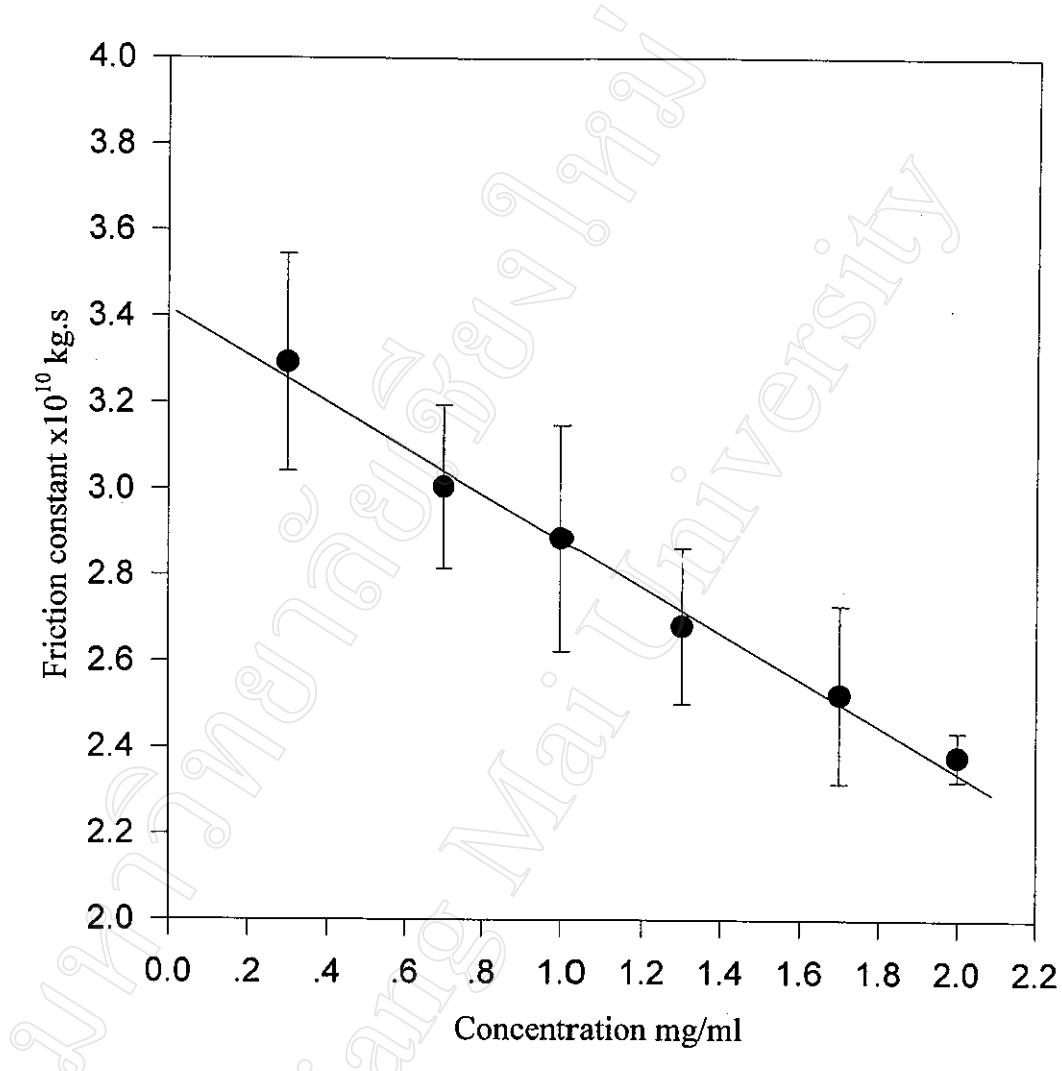


Figure 4.31 Plot of friction constant versus concentration of polystyrene  $M = 600000$  in cyclohexane at temperature  $42.4\text{ }^{\circ}\text{C}$

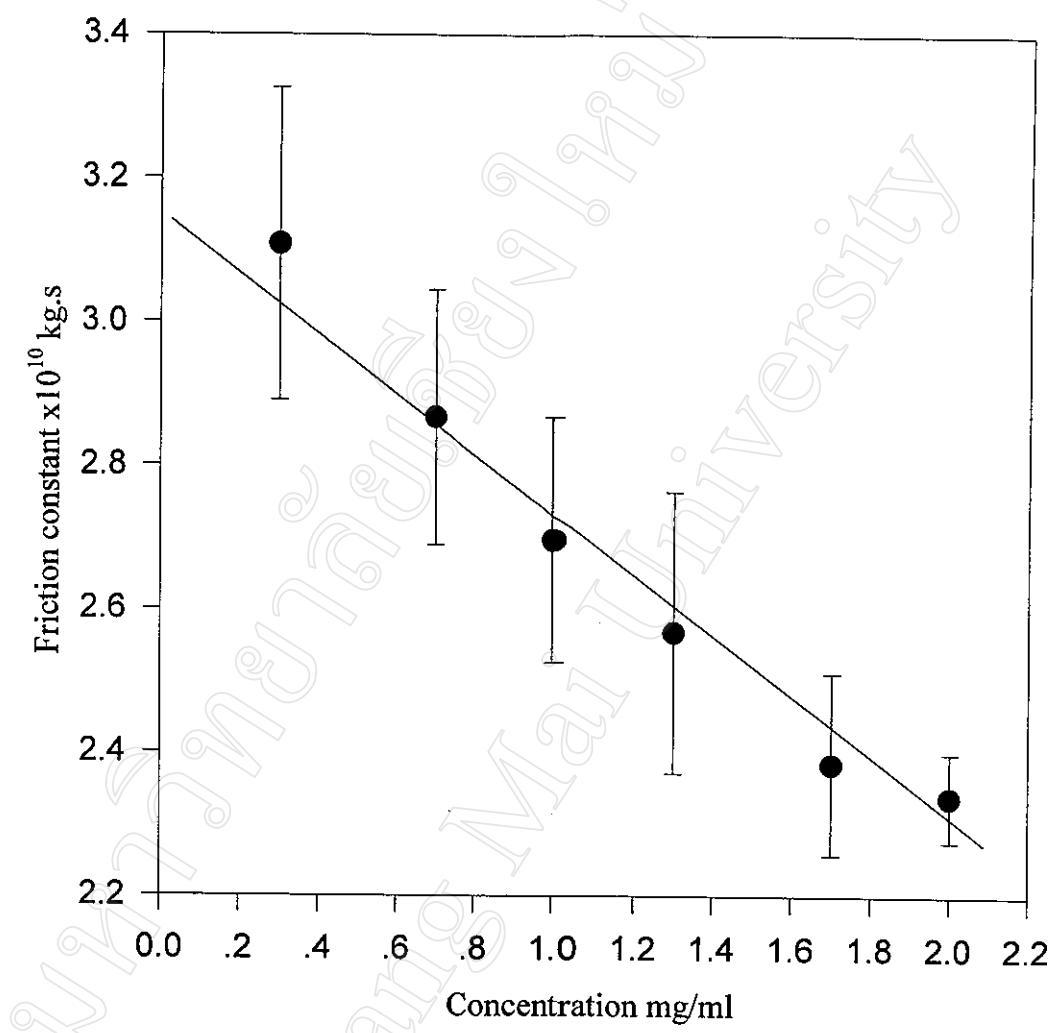


Figure 4.32 Plot of friction constant versus concentration of polystyrene  $M = 600000$  in cyclohexane at temperature  $44.7\text{ }^\circ\text{C}$

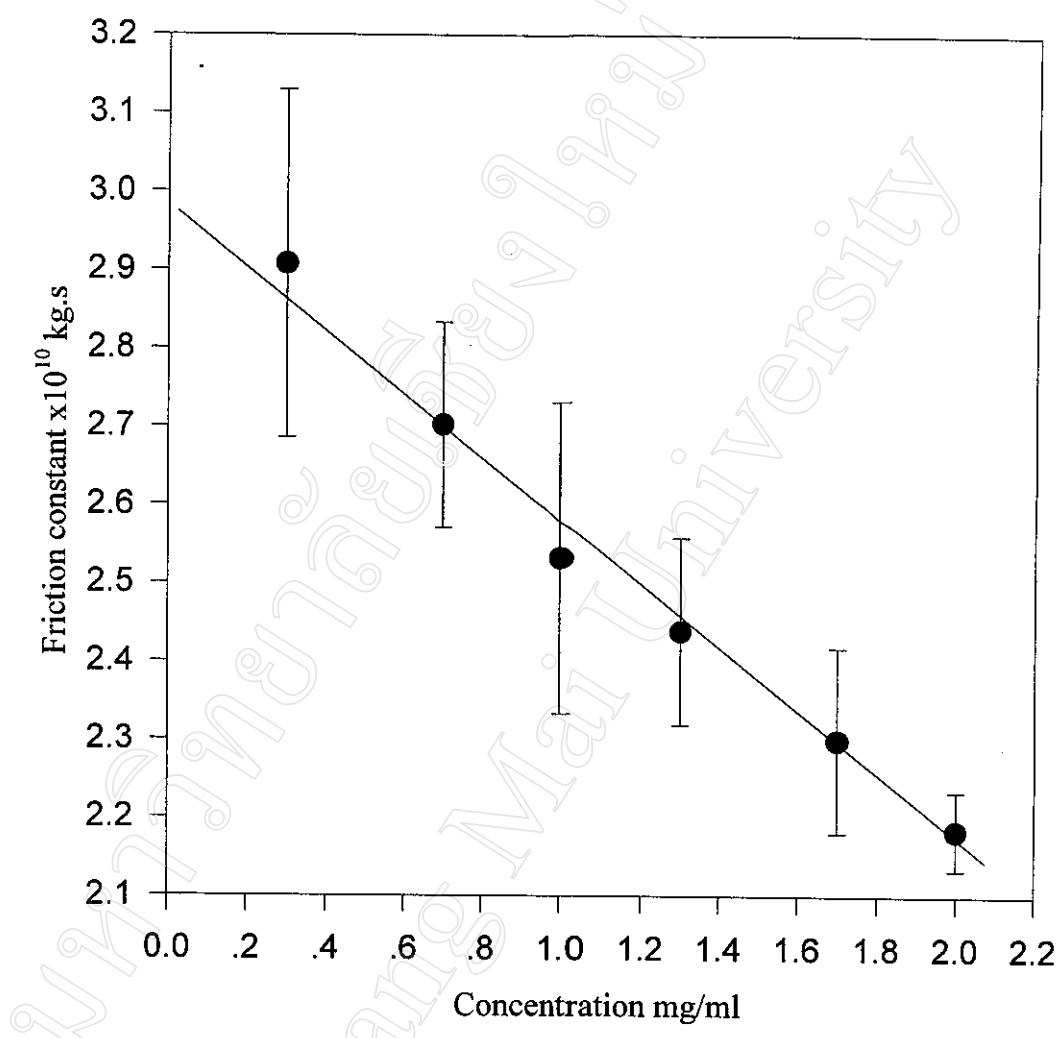


Figure 4.33 Plot of friction constant versus concentration of polystyrene  $M = 600000$  in cyclohexane at temperature  $47.2^\circ\text{C}$

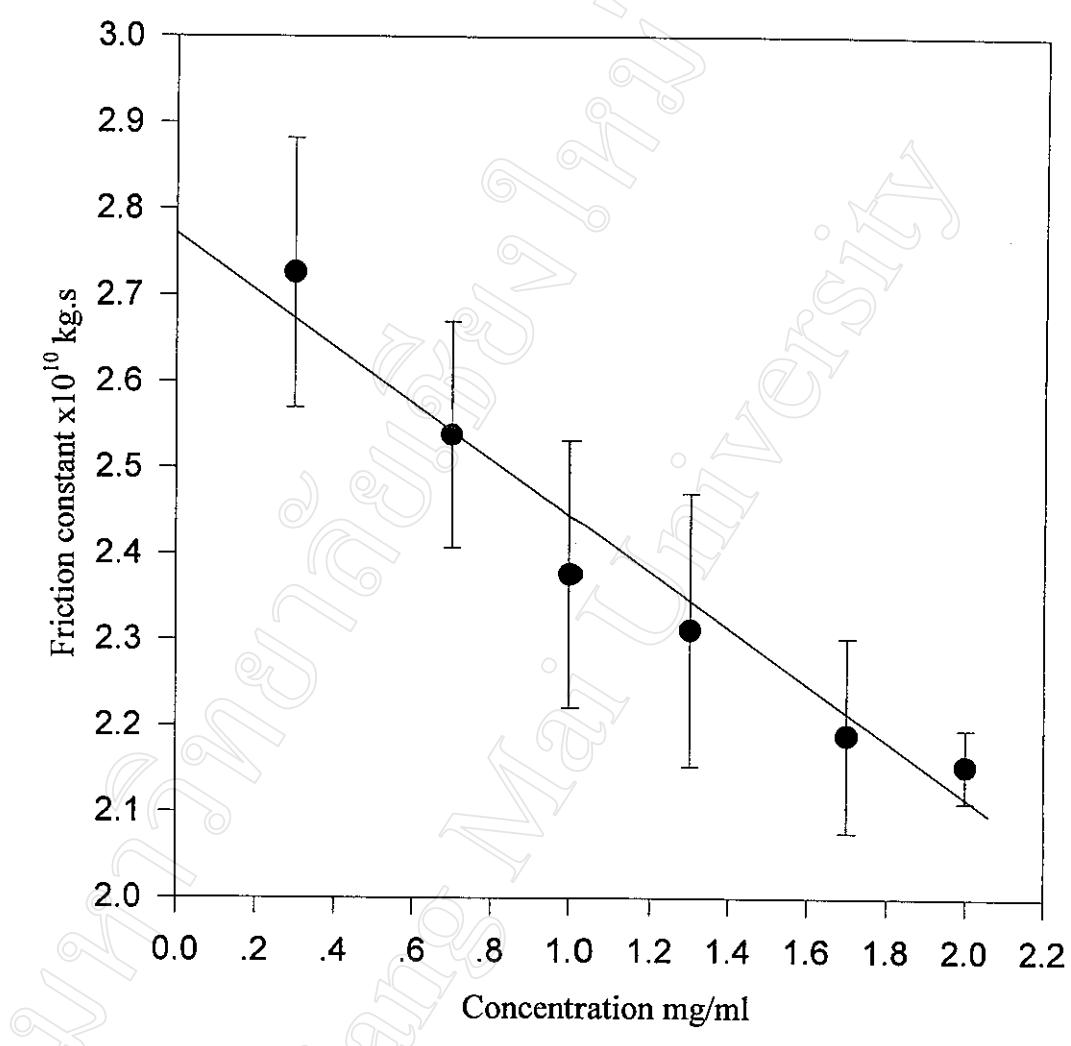


Figure 4.34 Plot of friction constant versus concentration of polystyrene M = 600000 in cyclohexane at temperature 49.8 °C