

CHAPTER III

RESULTS AND DISCUSSION

3.1 Molecular Characterization of the Polymer

3.1.1 Hydroxypropyl Cellulose

The HPC solutions were studied by viscometry and dynamic light scattering measurement. In this part, the effects of concentration dependence and molecular weight dependence were investigated.

(a) *Viscometry Measurement*

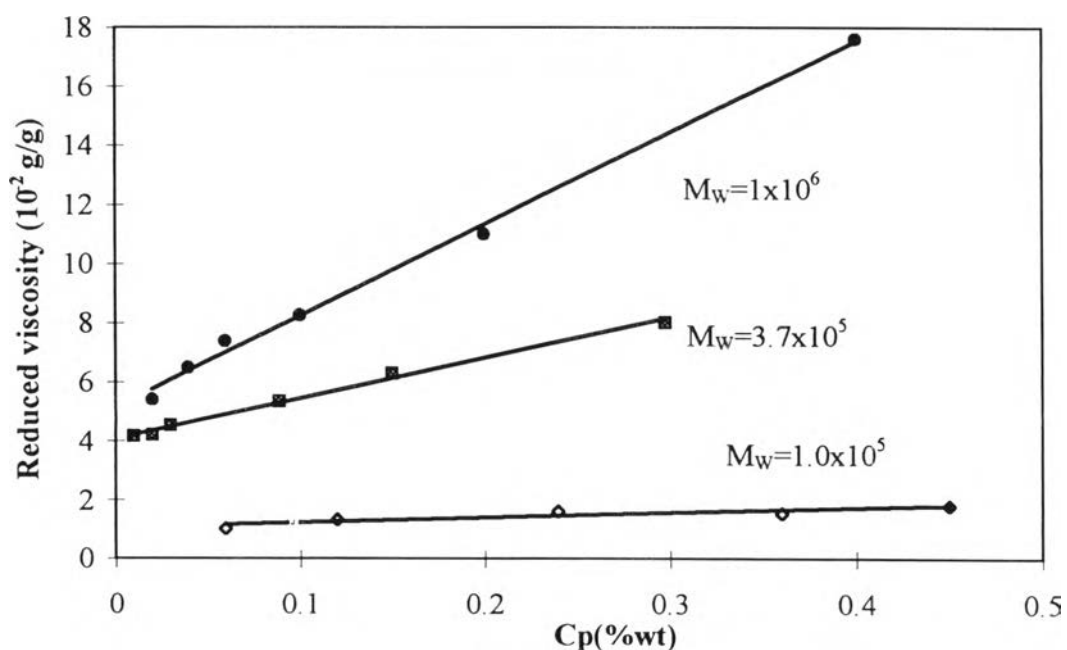


Figure 3.1 Reduced viscosity versus HPC concentration for 3 different molecular weights in water at 30°C.

Figure 3.1 shows the typical results of η_R as a function of HPC concentration, C_p at different molecular weights. It can be observed that η_R increases with polymer concentration for all three molecular weights. Their intrinsic viscosity, $[\eta]$, can be evaluated by extrapolating η_R or η_{sp} / C_p to zero concentration of polymer as expressed by the Huggins equation.

The critical concentration, C_p^* is the concentration at which the polymer chains begin to overlap each other; C^* can be defined by,

$$C^* = [\eta]^{-1}. \quad (3.1)$$

The C^* values are shown in table 3.1. The highest molecular weight has the lowest C^* that implies it forms an entangled polymer network more easily than the lower molecular weight.

(b) *Dynamic Light Scattering Measurement*

From fig. 3.2, diffusion coefficient (D) for the three HPC molecular weights slightly decreases with C_p . The value of apparent hydrodynamic radius ($R_{h, app}$) is inversely proportional to D so $R_{h, app}$ increases slightly with C_p . As expected, M_w has a significant effect on the D . The largest M_w has the lowest D and the highest R_h . D^0 values are shown in table 3.1

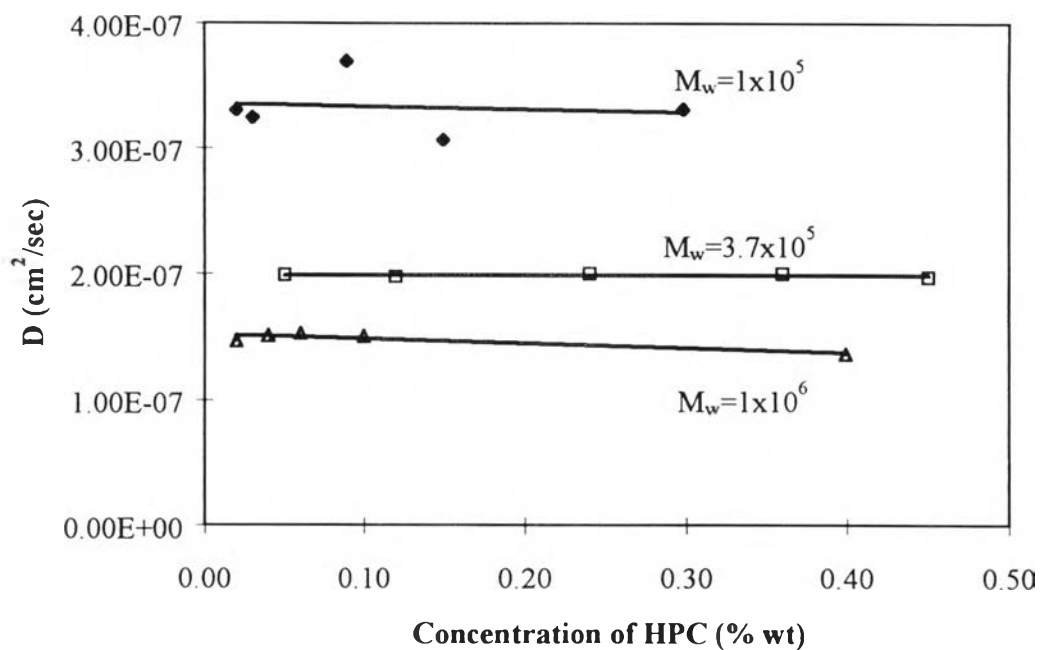


Figure 3.2 Diffusion versus concentration of HPC for 3 different molecular weights.

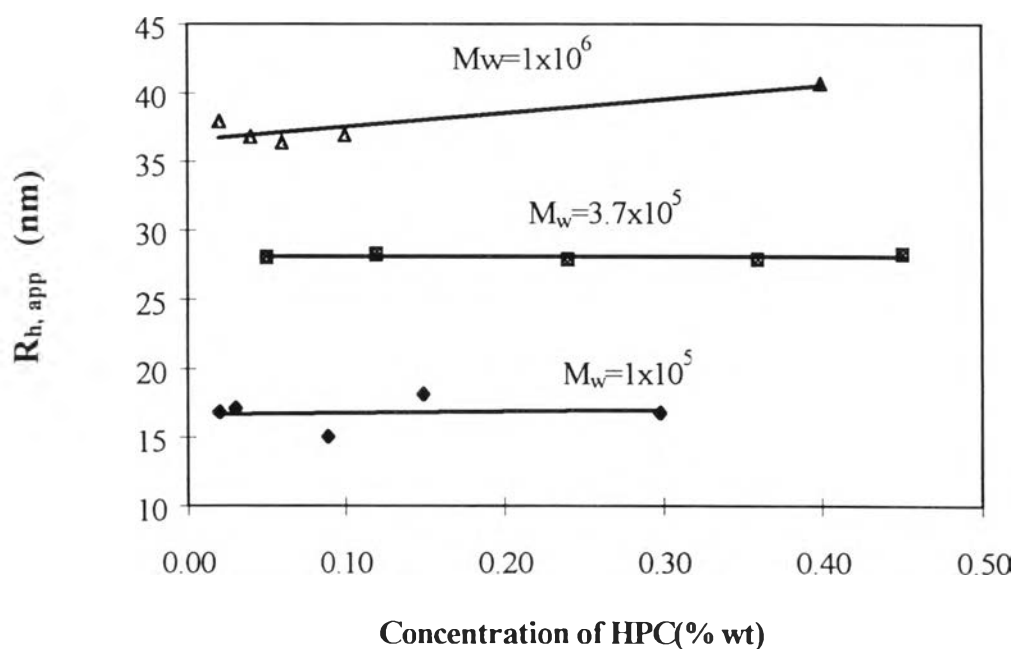


Figure 3.3 R_{h,app} versus concentration of HPC for 3 different molecular weights.

From figs. 3.1, 3.2 and 3.3, the values of $[\eta]$, C^* , D^0 and R_h for each HPC molecular weight are summarized in the table 3.1.

Table 3.1 The molecular properties of HPC solutions.

Mw. of HPC (g/mole)	$[\eta]$ (g/g)	C^* (g/100g)	$D^0 \times 10^8$ (cm ² /sec)	$R_{h, app}$ (nm)
1.0×10^5	105	0.95	16.70	16.7
3.7×10^5	407	0.27	9.92	28.0
1.0×10^6	513	0.20	7.62	36.5

The dependence on $\text{Log } M_w$ of HPC of $\text{Log } \eta$ and $\text{Log } D^0$ is shown in figure 3.4 and 3.5, respectively. The results are compared with the previous work (Yang and Jamieson, 1988).

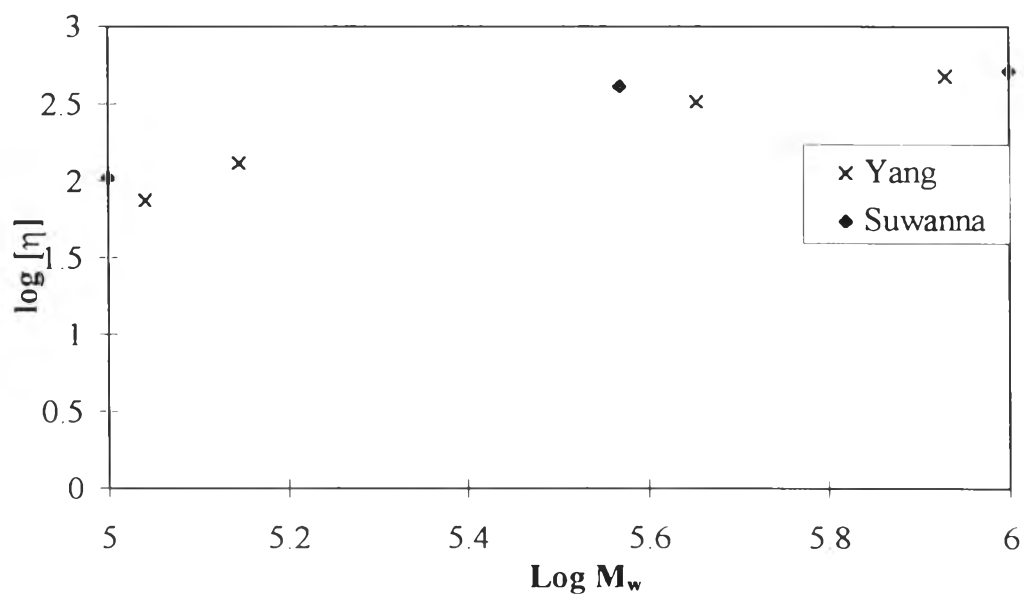


Figure 3.4 $\text{Log } [\eta]$ versus $\text{Log } M_w$ compared with Yang and Jamieson's data (1988)

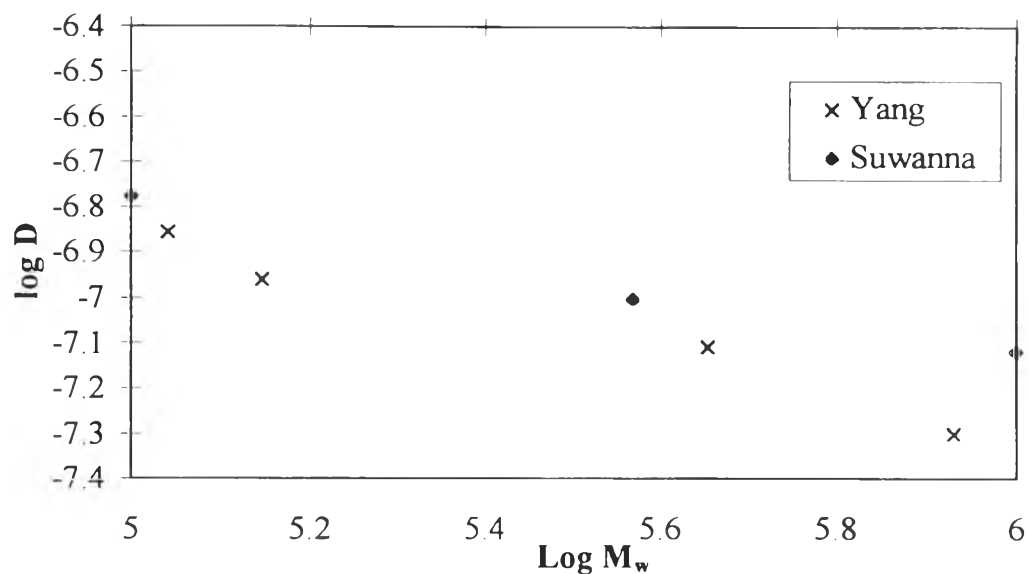


Figure 3.5 Log D^0 versus Log M_w compared with Yang and Jamieson's data (1988)

3.1.2 Polystyrene Latex

Dynamic light scattering measurements were made on dilute suspensions of polystyrene latex particles (in unit of ppm or 10^{-4} % by wt). When there is no mutual interaction or zero concentration dependence, D value corresponds to that of an isolated sphere. The hydrodynamic radius, R_h of latex can be obtained from the Stokes-Einstein equation (eq. 2.21). From fig. 3.6, D^0 and diameter of latex spheres are summarized in table 3.2.

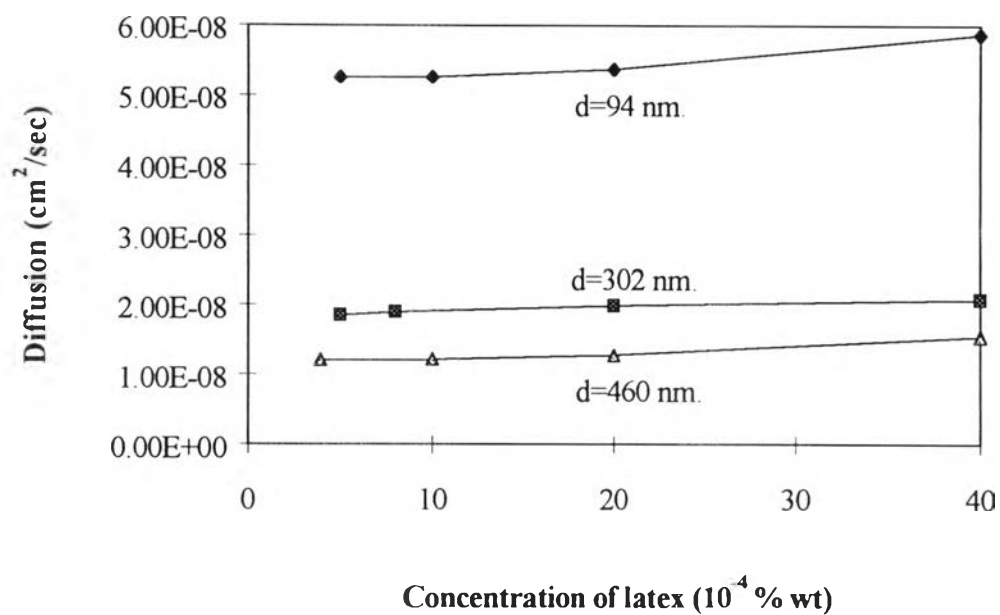


Figure 3.6 Diffusion of the Polystyrene sphere in water at 30⁰C.

Table 3.2 Diffusion of the Polystyrene latex sphere in water.

Diameter (nm) as quoted	D ₀ (cm ² /sec)	Diameter (nm) from DLS
94	5.21x10 ⁻⁸	106.9
302	1.84x10 ⁻⁸	302.3
460	1.19x10 ⁻⁸	469.3

The next part will describe the effect of Triton X-100, molecular weight and concentration of HPC and latex diameter on the diffusion coefficient (D) of polystyrene sphere in the HPC solutions.

3.2 Effect of Latex Diameter and Triton X-100 Concentration

Figure 3.7 represents the diffusion coefficient (D) of the latex spheres (0.001 % wt, with diameter 302 and 460 nm) in HPC solutions (0.4 % wt, $M_w = 100,000$) as a function of Triton X-100 concentration (C_x). The diameter of the spheres can be determined by the Stoke-Einstein equation. By replacing η_s with the bulk viscosity of HPC, the diameter of the spheres was obtained. The influence of C_x on the apparent latex diameter is shown in fig. 3.8.

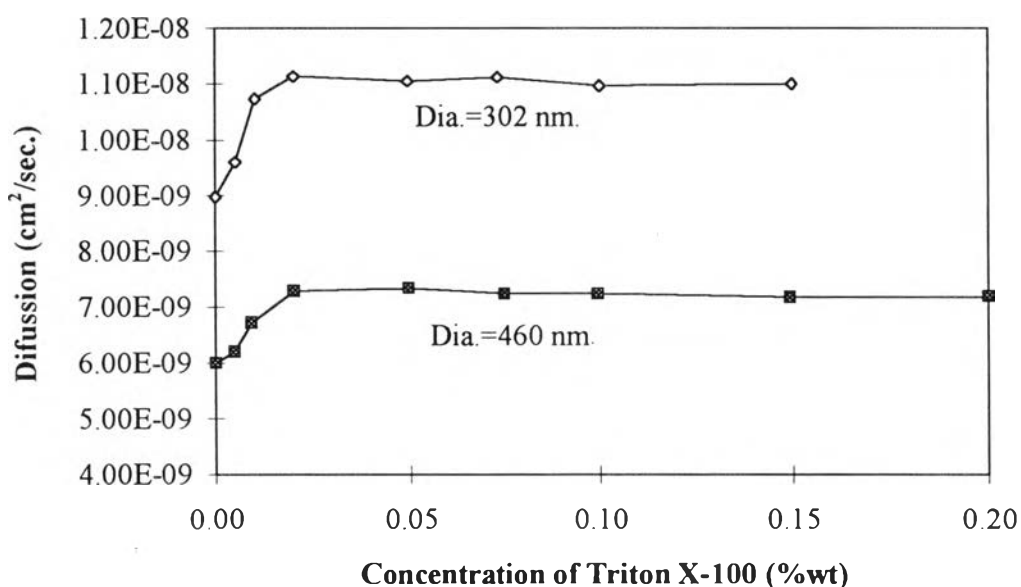


Figure 3.7 Diffusion versus concentration of Triton X-100 for latex spheres (0.001 % wt, with diameter 302 and 460 nm) in 0.4 % wt HPC ($M_w = 100,000$) solution.

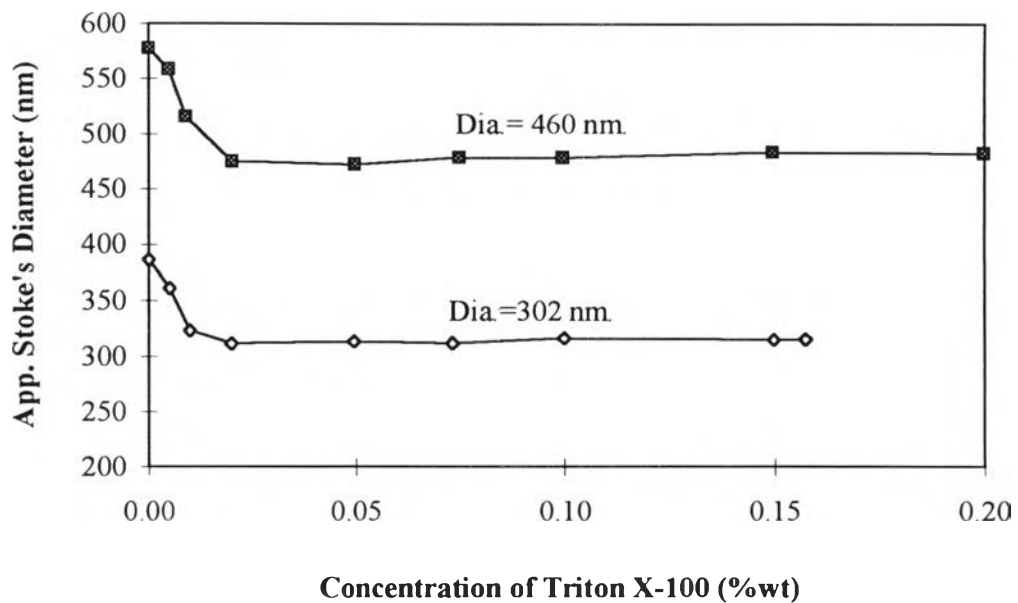


Figure 3.8 Apparent diameter versus concentration of Triton X-100 for latex spheres (0.001% wt., with diameter 302 and 460 nm) in 0.4 % wt of HPC ($M_w=100,000$) solution.

In the absence of Triton X-100, HPC molecules adsorb onto latex surface due to a hydrophobic interaction leading to a higher diameter from bare diameter. The spheres with adsorbed layer of HPC have smaller D values. But when Triton X-100 was added into the system, D increased sharply with C_x at the first time and then became constant at higher C_x . This is because the Triton X-100 can adsorb on the latex surface and inhibit the adsorption of HPC to latex. The interaction strength between HPC and latex was weakened resulting in a smaller layer thickness (δ) and higher D. The amount of Triton X-100 that are needed to adsorb on the latex size 302 and 460 nm. are 18 and 20 weight ratio of Triton X-100 : Latex, respectively. The large size of sphere requires a larger amount of Triton X-100 because of its higher surface area. When the system had an excess concentration of Triton X-100, the adsorption of HPC on latex was completely inhibited. The situation resembled the diffusion of a bare sphere through the polymer matrix.

Addition of Triton X-100 at a concentration of 0.05 % to the latex suspension apparently completely inhibits the adsorption of HPC, the latex diameter being some 10 nm larger than that value in bare sphere. The Triton X-100 or (p-1,1,3,3-tetramethylbutyl phenoxy) poly(oxyethylene glycol) has an oxyethylene chain length, when fully extended, of about 34 °A (Robson and Dennis, 1977) and the octylphenyl chain length of about 10 °A. This would suggest that the adsorption of Triton X-100 is an extended configuration (Brown and Rymden 1986). Figure 3.7 represents the schematic picture of the adsorption of the Triton X-100 on polystyrene latex as proposed by Piirma, I. and Chen, S-R. (1980)

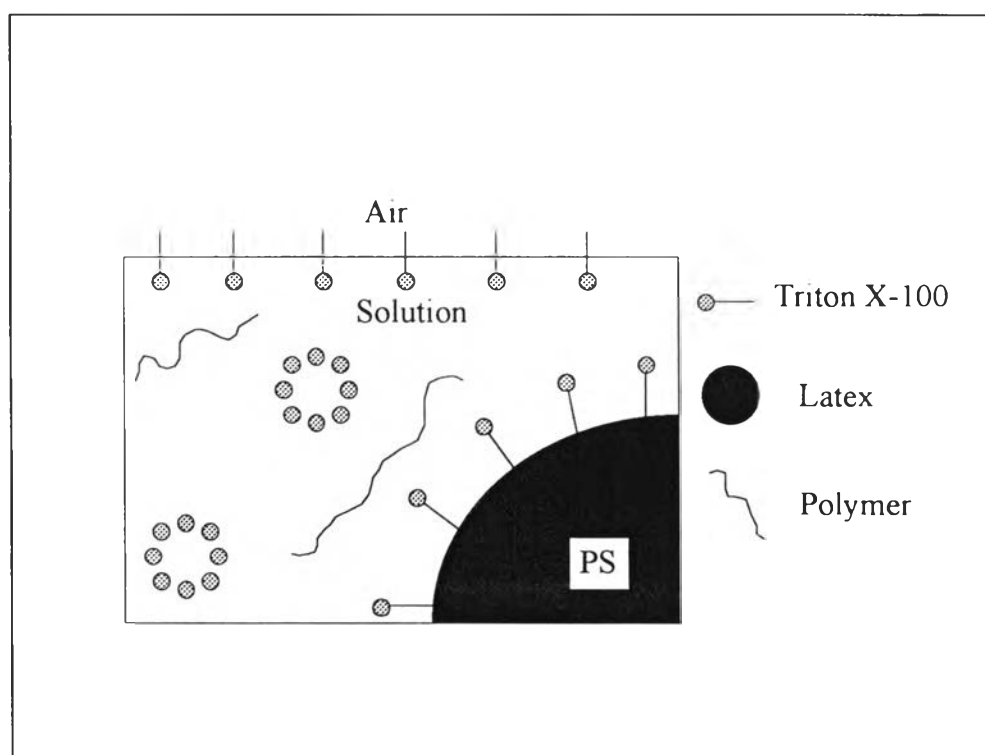


Figure 3.9 The adsorption of Triton X-100 on polystyrene sphere in HPC solution with 0.05 % of Triton X-100. (Piirma, I. and Chen, S-R., 1980)

From fig. 3.9, the water-insoluble hydrophobic tails of Triton X-100 adsorb on the latex sphere by hydrophobic attraction. At any instant an equilibrium exists between the adsorbed surfactant molecules, the freely moving ones in the aqueous phase, and the ones adsorbed on the latex particles (Irja et al., 1980). Because of the quite large diameter of latex, only single mode of DLS was detected that referred to scattering from particle with adsorbed layer. The scattering from polymers and surfactant molecule were negligible at dilute concentration.

3.3 The Effect of Molecular Weight of HPC

For sphere with diameter 94 nm, in HPC $M_w = 370,000$ and $1,000,000$ showed bimodal fits in multimodal analysis. Multimodal analysis of the time correlation function gives a binomial fit which contains a fast mode and a slow mode. Brown and Rymden (1986) found that the fast mode which indicated the diffusion of the latex monomer. The slow mode corresponds to aggregate species with diffusion about 2 times slower than that of the latex monomer as shown in fig. 3.10. The aggregation behavior is consistent with a bridging mechanism as shown in fig. 1.5. In this work the difference in diffusion should come from the wide particle distribution means that the structure of adsorbed layer on each particle is different and also because of a wide molecular distribution of HPC.

Figure 3.11 shows the diffusion of latex sphere with diameter 96 nm as a function of C_x for the three molecular weights of HPC by fixing polymer concentration (C_p) at 0.2 % wt (in the dilute regime). It shows the same trend for all 3 molecular weights, D increases with C_x because the adsorption of HPC onto latex sphere was inhibited by Triton X-100 and after 0.015 % wt of

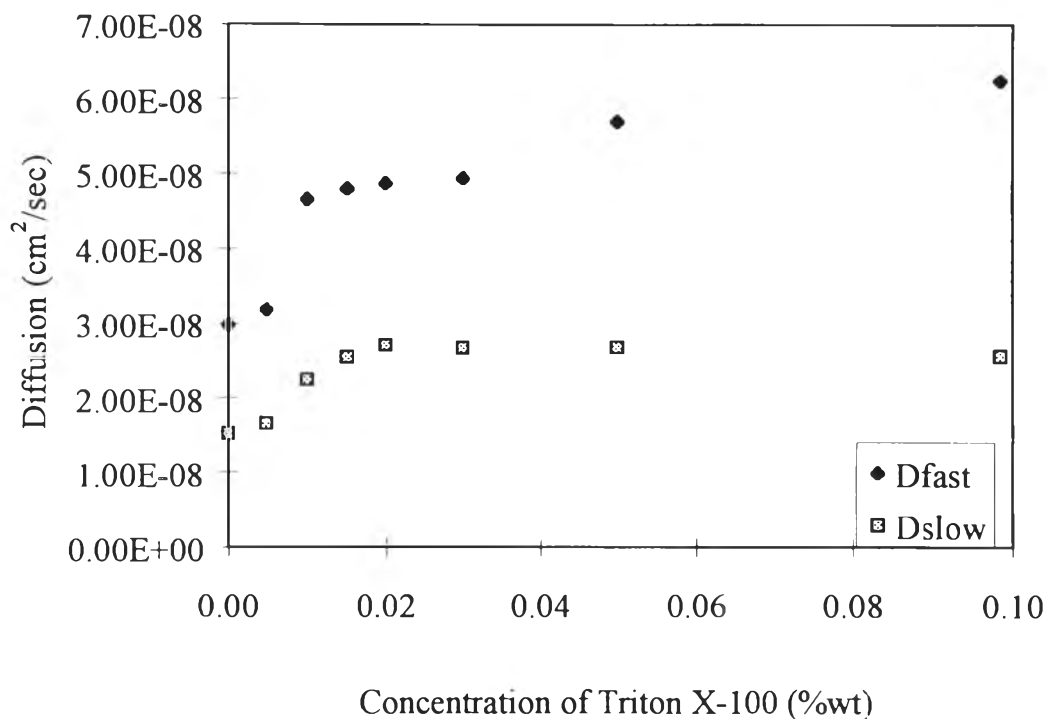


Figure 3.10 Diffusion in fast mode (D_{fast}) and slow mode (D_{slow}), of 0.001 % wt of latex (diameter 94 nm) in 0.2 % wt. of HPC ($M_w=10^6$) solution.

Triton X-100, D seems to be constant as already mentioned in chapter 3.2. The highest molecular weight of HPC shows the lowest D for the whole range of C_x because of the hydrodynamic drag force and the obstacle effect. The relation between the Stoke's diameter and C_x can be shown in fig. 3.12. Note that, in calculating the diameter, we used the viscosity of the 0.2 % wt of HPC solution [for $M_w = 100,000$, $\eta = 1.2 \text{ mN.m}^{-2}$, for $M_w = 370,000$, $\eta = 2.1 \text{ mN.m}^{-2}$ and for $M_w = 1,000,000$, $\eta = 2.6 \text{ mN.m}^{-2}$]. Above 0.015 % wt of C_x , the diameter is close to the bare diameter of the sphere in low molecular weight of HPC ($M_w = 100,000$).

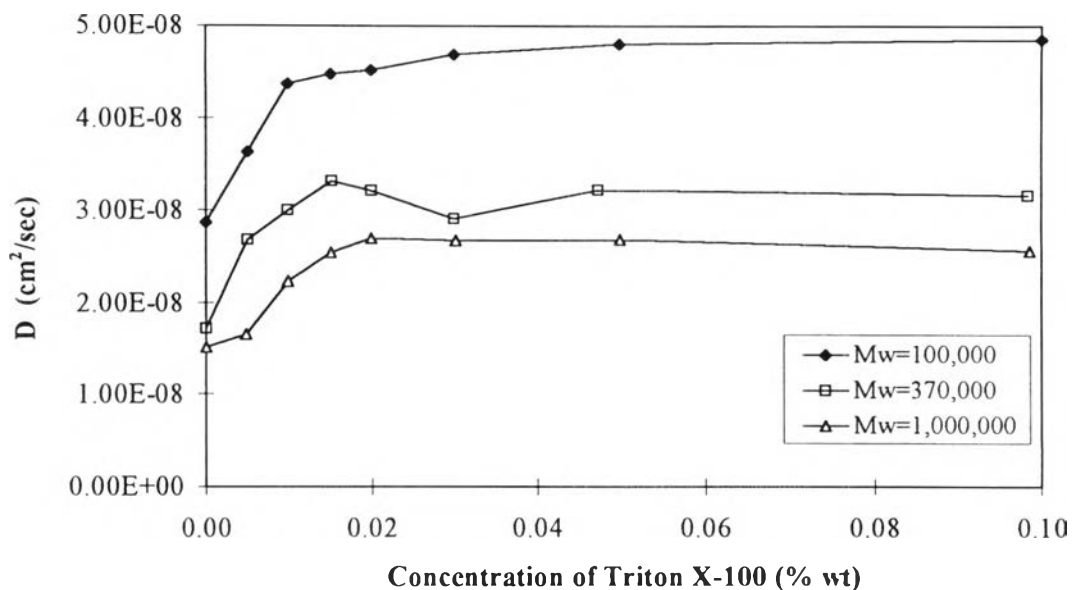


Figure 3.11 The molecular weight dependent diffusion coefficient as a function of Triton X-100 concentrations (fixed $C_p = 0.2$ % wt, latex diameter = 94 nm and $C_{\text{latex}} = 0.001$ % wt.)

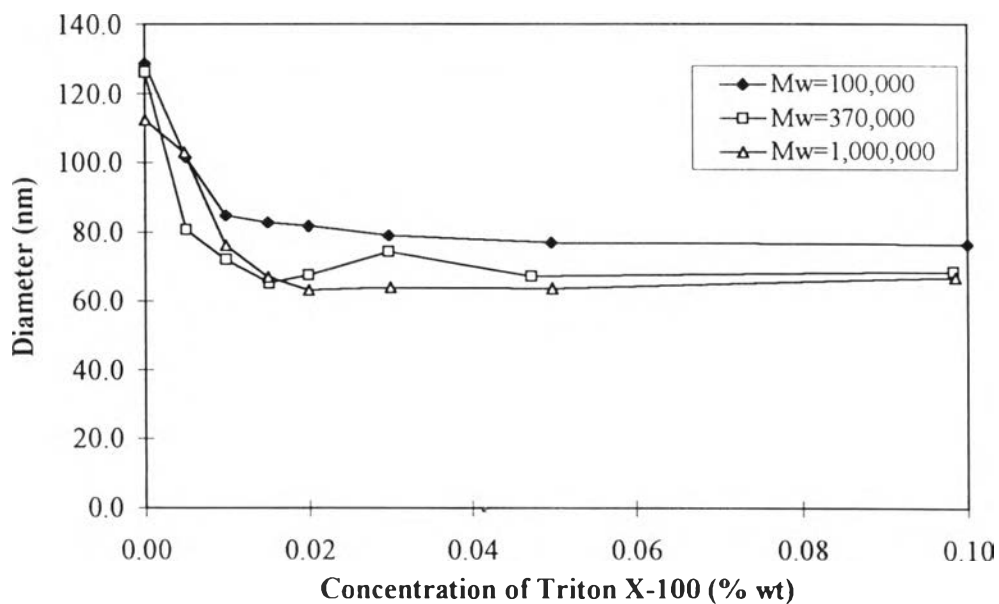


Figure 3.12 The molecular weight dependent sphere diameter as a function of Triton X-100 concentrations (fixed $C_p = 0.2$ % wt, latex diameter = 94 nm and $C_{\text{latex}} = 0.001$ % wt)

3.4 Effect of Polymer Concentration and Triton X-100.

3.4.1 Compare the Diffusion of latex in HPC Solution with 0 % and 0.10 % of Triton X-100

Figure 3.13 and 3.14 represent the diffusion of latex of diameter 460 nm in solution of three molecular weights of HPC, with 0 % and 0.1 % wt. of Triton X-100, respectively (plotted by using fast mode). In the absence of Triton X-100, D decrease sharply with C_p because HPC adsorbs on latex sphere inducing the higher layer thickness of spheres. Moreover the additional drag force comes from the increase in viscosity of the solvent, so D for HPC $M_w=10^6$ is the highest. Now we consider the effect of each molecular weight with and without has 0 % wt. and 0.1 % wt. of Triton X-100, as shown in figs. 3.15 ,3.16 and 3.17. D in 0.1 % wt. is higher that in 0 % wt. of Triton X-100. The result is that 0.1 % wt. of Triton X-100 is the excess concentration that it can adsorb on the whole surface of latex and completely inhibit the adsorption of HPC on the latex. The decrease of D in 0.1 %wt corresponds to the diffusion of sphere with a surfactant layer in the entangled polymer matrix.

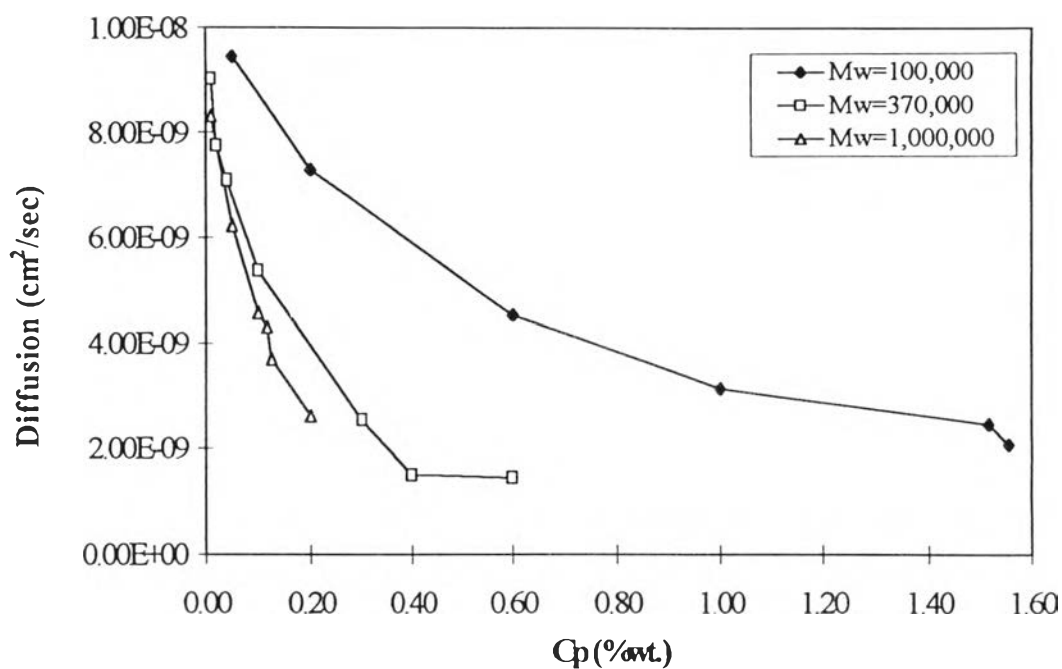


Figure 3.13 The dependence on HPC molecular weight of the diffusion of latex sphere of diameter 460 nm without Triton X-100.

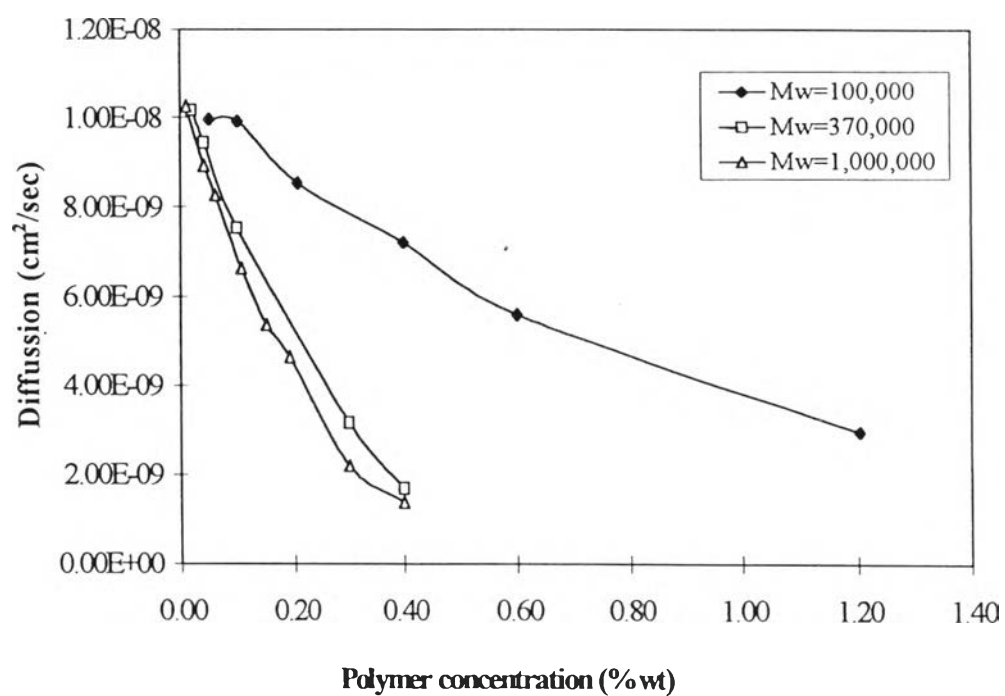


Figure 3.14 The dependence on HPC molecular weight of the diffusion of latex sphere of diameter 460 nm with 0.1 % wt. Triton X-100.

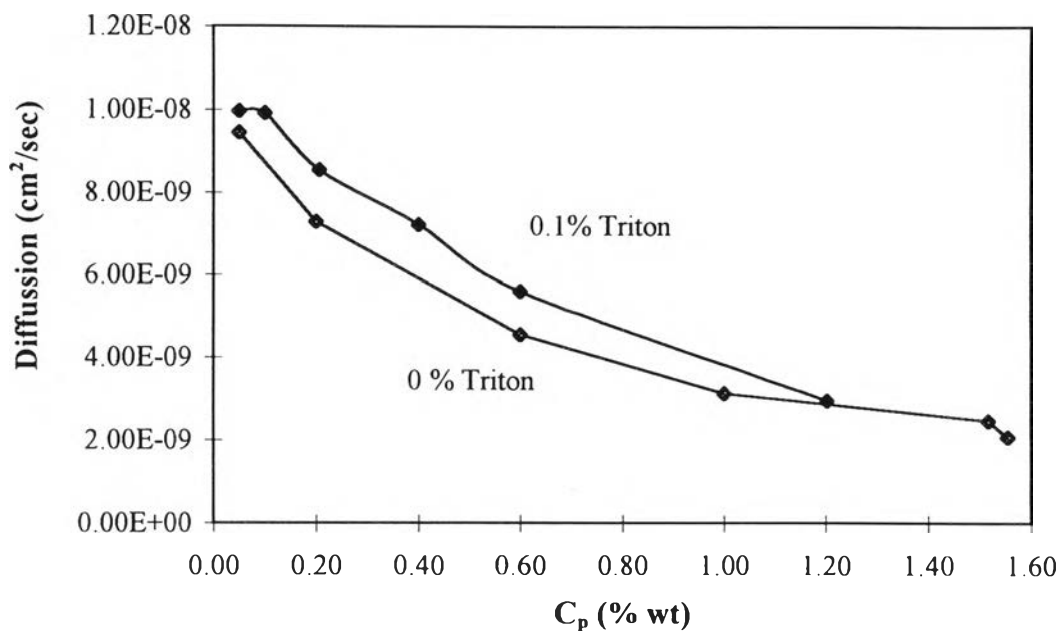


Figure 3.15 Comparison between the diffusions of latex sphere (diameter 460 nm) in HPC ($M_w=10^5$) solutions with 0 % and 0.1 % wt of Triton X-100.

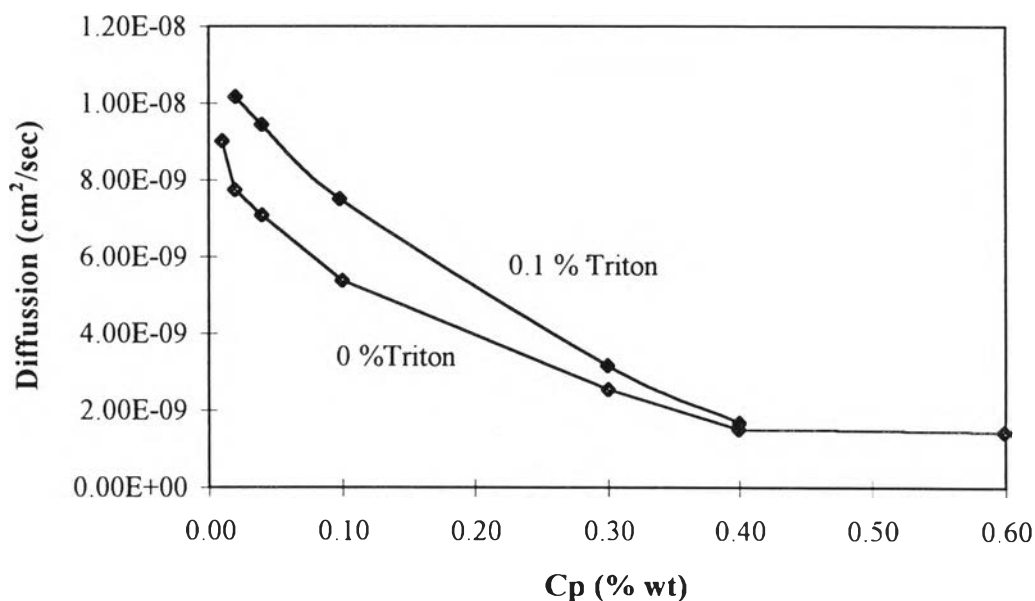


Figure 3.16 Comparison between the diffusions of latex sphere (diameter 460 nm) in ($M_w=3.7 \times 10^5$) solutions with 0 % and 0.1 % wt. of Triton X-100.

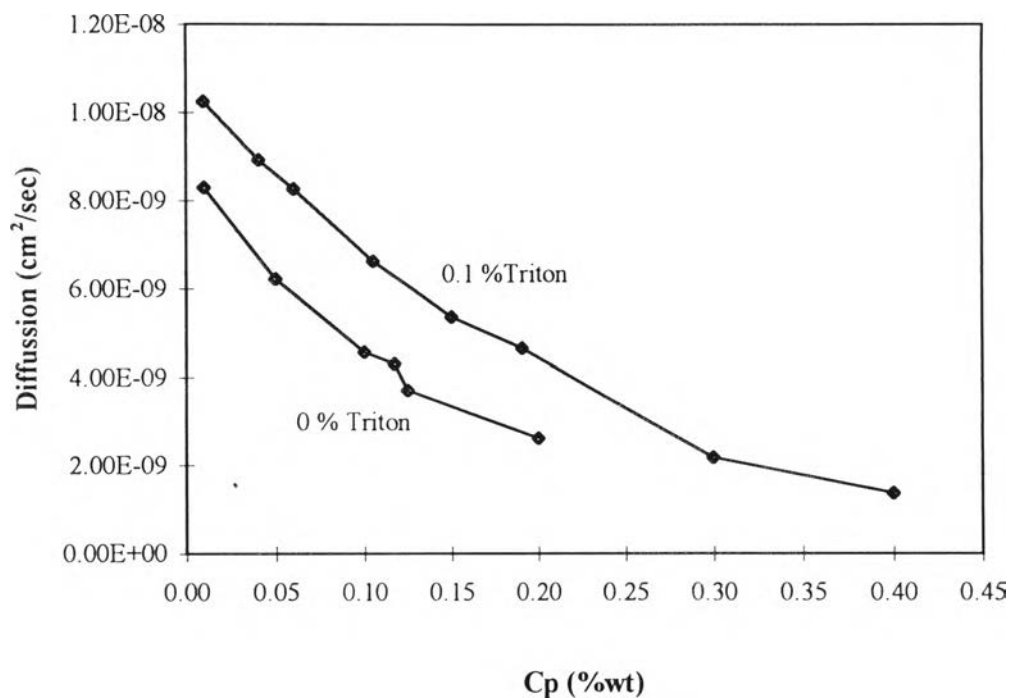


Figure 3.17 Comparison between the diffusions of latex sphere (diameter 460 nm) in HPC ($M_w=10^6$) solutions with 0 % and 0.1 % wt. of Triton X-100.

3.4.2 Scaling Exponent Determination

The diffusion of sphere in polymer matrix can be described by the stretched exponential function in the form of

$$D/D_0 = \text{EXP}(-AC^\delta), \quad (3.2)$$

where δ is the scaling exponent, and A is the concentration coefficient. δ can be determined by the slope of $\ln(\ln(D/D_0))$ versus C_p as shown in fig. 3.18 and fig. 3.19.

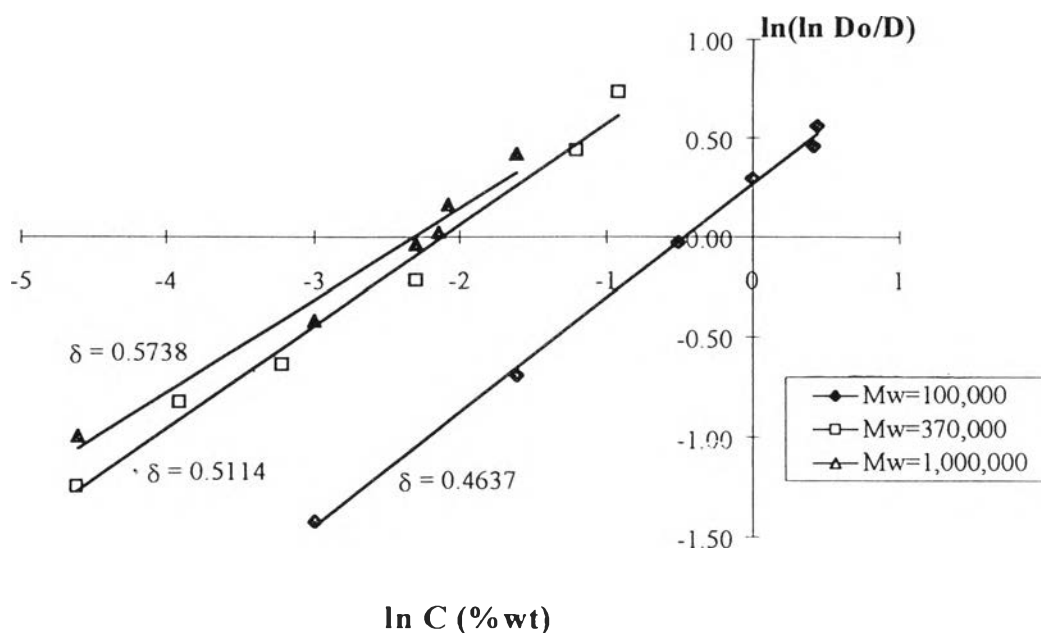


Figure 3.18 Determination of δ values of the 460 nm latex in HPC solution in the absence of Triton X-100.

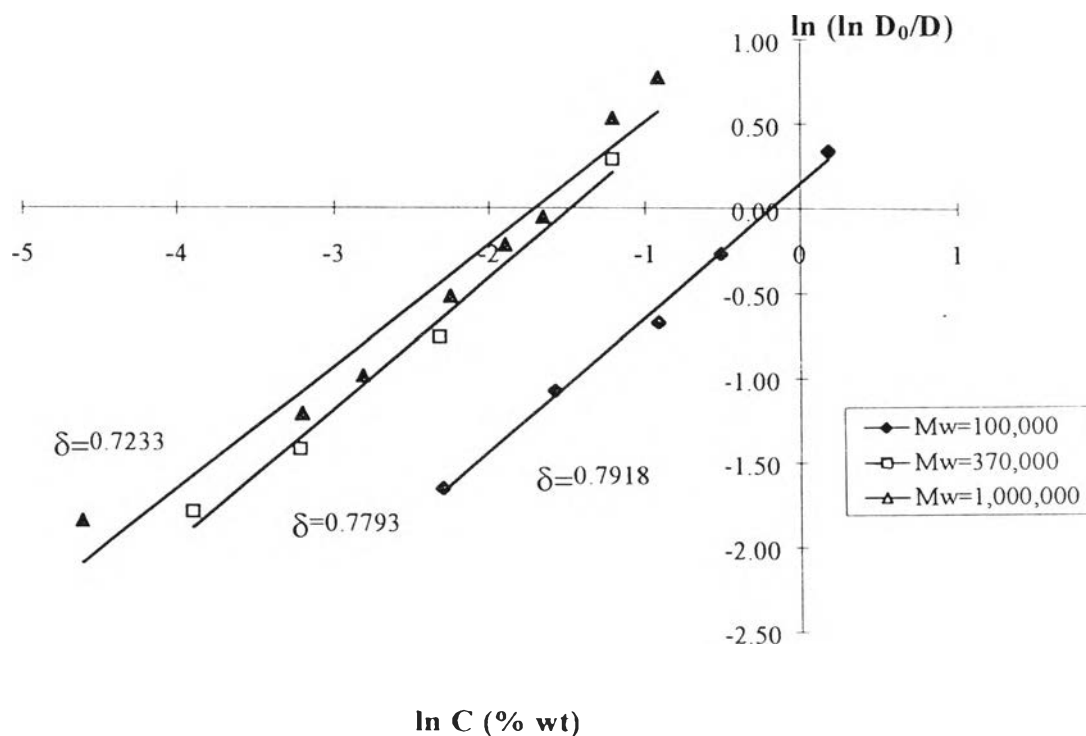


Figure 3.19 Determination of δ values of the 460 nm latex in HPC solution in the presence of 0.1 % wt. of Triton X-100.

Table 3.3 The effect of added Triton X-100 and molecular weight of HPC on the scaling exponents

Mw. of HPC	0 % wt of Triton X-100		0.1 % wt of Triton X-100	
	δ	A	δ	A
1.0×10^5	0.57	1.31	0.79	1.15
3.7×10^5	0.51	2.92	0.77	3.73
1.0×10^6	0.46	2.95	0.72	3.44

From table 3.3, δ values for the three M_w of HPC in case of 0 % Triton X-100 show that the highest value of δ value belongs to HPC with $M_w=10^5$ g/mole. δ values are smaller for $M_w=3.7 \times 10^5$ and 1×10^6 respectively. The reason is the stronger steric effect from the chain layer of absorbed HPC and the higher bulk viscosity. At 0.1 % of Triton X-100 represents the excess concentration that surfactant will adsorb on the whole surface of latex spheres. The δ values shift up in comparison with those in the absence of Triton X-100 at the same M_w . This implies that the added Triton X-100 affects the interaction between latex and absorbed HPC by reducing the layer thickness, resulting in the higher values of δ .

However, molecular weight effect with 0.1 % Triton X-100 should not show a significant change because of the binding effect of added surfactant on the whole surface; their diffusions should be those of the bare spheres. From table 3.3, δ values of $M_w=10^5$ and 3.7×10^5 is nearly the same but $M_w=10^6$ is quite lower. Because δ is sensitive to diffusion of the system so the lower

value in the case of $M_w=10^6$ may be come from the more obstruction from HPC matrix in the semidilute regime.

3.4.3 Viscosity Data (Effect of Triton X-100)

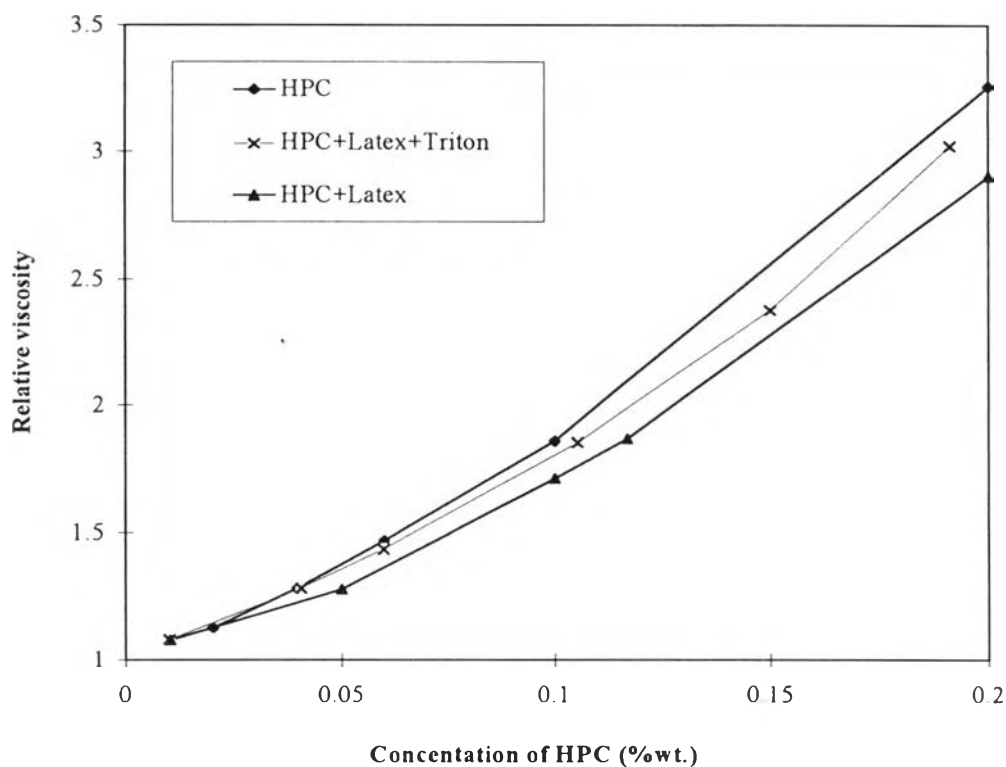


Figure 3.20 Relative viscosity of three systems:

- a) Only HPC ($M_w=1,000,000$).
- b) Latex in HPC with 0.1 % wt. of Triton X-100
- c) Latex in HPC without Triton X-100

From figure 3.20, we compare the relative viscosity at various C_p . The highest viscosity belongs to the system of HPC alone then latex in HPC with 0.1 % wt. of Triton X-100 and latex in HPC with 0% wt of Triton X-100, respectively. This observation agrees with the DLS data; adding Triton X-100 will reduce the interaction between latex and HPC, inducing a higher

diffusion of sphere and lowering viscosity of the mixture because a higher number molecules of the free polymers are left in the system.