

## Effect of associating polymer on the dispersion stability and rheology of suspensions

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### Abstract

Associating polymers are hydrophilic long-chain molecules to which a small amount of hydrophobic groups (hydrophobes) is incorporated. In aqueous solution, the association interactions result in the formation of three-dimensional network through flowerlike micelles at high concentrations. In colloidal suspensions, the associating polymers act as flocculants by bridging mechanism. The rheological properties of suspensions flocculated by associating polymers end-capped with hydrophobes are studied in relation to the bridging conformation. At low polymer concentrations, the polymer chains effectively form bridges between particles by multichain association. The suspensions are highly flocculated and show typical viscoelastic responses. When the polymer concentration is increased above the adsorbance at saturation, the excess polymer chains remaining in the solution phase build up three-dimensional network by associating interactions. Since the presence of particles does not significantly influence the network structures in the medium, the relative viscosity, which gives a measure of the degree of flocculation is decreased with increasing polymer concentration. The bridging conformation and flocculation level vary strongly depending on the polymer concentrations.

**Keywords** : associating polymers, suspension rheology, dispersion stability, reversible bridging, three-dimensional network

### 1. Introduction

In polymer adsorption at a solid-liquid interface, only a portion of segments of the polymer chain is in direct contact with the surface, while the rest extend away from the surface into the solution. When adsorbed to the surface of a colloidal particle, polymers can either flocculate or stabilize the suspension, depending on the surface coverage. Below the saturation coverage, the long loops extending from particles with adsorbed layers can attach to the surface of bare particles. When the polymer chain adsorbs onto two or more particles and causes flocculation, the effect is referred to as bridging flocculation (Iler, 1971; Fleer and Lyklema, 1974). The suspensions flocculated by polymer bridging show shear-thinning flow at low shear rates and elastic responses at low frequencies (Otsubo and Watanabe, 1988; Otsubo, 1990). The shear-thinning flow can be explained by the shear-induced breakdown of floc structure and the elasticity by the existence of three-dimensional network. Polymer adsorption is generally irreversible because polymer chain may attach to the surface at

several points and not be able to desorb simultaneously from all sites. Therefore, the highly flocculated suspensions show plastic behavior with an infinite relaxation time.

In many processes such as paint production and magnetic coating, various types of polymers are used as rheology control agents. However, the traditional polymers are not sufficient to satisfy the requirements of high viscosity with Newtonian flow profiles in a wide range of shear rates. Recently associating polymers receive increasing interests as thickeners. The interest stems from the need in industries to accurately control the suspension viscosity under a variety of shear conditions. The associating polymers consist of water-soluble backbone to which a small amount of hydrophobic groups (hydrophobes) is incorporated. In aqueous solution, the hydrophobes tend to aggregate and create three-dimensional network which gives rise to interesting rheological effects (Jenkins *et al.*, 1991; Wang *et al.*, 1996; Jimenez-Regalado *et al.*, 2000). In the case of suspensions, the associating polymers act as flocculants, because the hydrophobes can simultaneously adsorb onto two particles. The suspensions can be flocculated by bridging (Sperry, 1987) at low polymer concentrations and by depletion at relatively high concentrations (Santore *et al.*, 1990a; 1990b). Depending on the population of hydro-

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phobes per molecule and adhesion energies for hydrophobe-hydrophobe and hydrophobe-surface, the suspensions are flocculated by different mechanisms.

In a previous paper (Horigome and Otsubo, 2002), we studied the rheological properties of suspensions flocculated by bridging of associating polymers. The most interesting finding is that the rheological values such as viscosity, elasticity, and relaxation time, are not given by a simple function of polymer concentration, although the polymer chains are considered to contribute to the bridging of particles. Through the rheological measurements and sedimentation experiments, two bridging models are derived. One is the direct bridging of single chain, in which one polymer chain is adsorbed onto two particles to bind them together. The other is the multichain bridging, in which the particles are connected by linkage of interchain associations. The conformation of adsorbed polymer and mechanical properties of bridges strikingly vary with the particle and polymer concentrations. The present study is designed to provide more insight into the flocculation induced by associating polymer chains. The attention is focused to the relation between suspension rheology and bridging conformation.

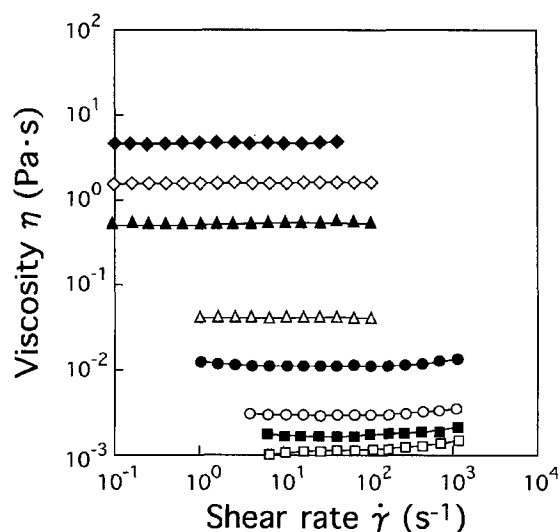
## 2. Experimental

### 2.1. Samples

The suspensions were composed of polystyrene particles, associating polymer, and water. The polymer particles with a diameter of 124 nm were formed by emulsion polymerization. The stock suspension without polymers was electrostatically stabilized. The associating polymer was hydrophobically modified ethoxylated urethane (HEUR) (RM-825 from Rohm and Haas), the molecular weight of which was about  $2.5 \times 10^4$ . The hydrophobes are incorporated on the ends of molecules as terminal groups. The suspensions were prepared at particle concentrations of 10% and 30% by volume. The concentration of associating polymer was in the range of 0–5.0% by weight based on the water. The rheological measurements were carried out after the suspensions were stored under gentle shear on a rolling device for one week.

### 2.2. Measurements

Steady-shear viscosity, creep behavior, and dynamic viscoelasticity were measured using a parallel plate geometry on a stress-controlled rheometer (Haake Rheo-Stress RS100). The diameter of plates was 35 mm and the gap between two plates was 0.8 mm. The surfaces of both plates were serrated to prevent wall slip. By combining the steady-flow and creep measurements, the viscosity was determined in the range of shear rates from  $2.0 \times 10^{-5}$  to  $3.0 \text{ s}^{-1}$ . The dynamic viscoelastic functions ( $G'$ ,  $G''$ ) were measured as a function of frequency at small strains in the lin-



**Fig. 1.** Shear rate dependence of viscosity for aqueous solutions of HEUR polymer: 0.20(□), 0.35(■), 0.50(○), 0.75(●), 1.0(△), 2.0(▲), 3.0(◇), 5.0 wt%(◆).

ear regions. The frequencies were from  $8.9 \times 10^{-2}$  to  $6.3 \times 10^1 \text{ s}^{-1}$ . The temperature was  $25^\circ\text{C}$  for all runs.

The suspensions were stored at rest for sedimentation. The final sedimentation volume gives the concentration of the dispersed phase, from which the surface separation in the flocs can be determined. The amount of polymer adsorbed on the particles was also calculated from the viscosity of supernatant solution.

## 3. Results and discussion

### 3.1. HEUR solutions

Figure 1 shows shear rate dependence of viscosity for aqueous solutions of HEUR polymer. The flow can be approximated as Newtonian in the entire range of shear rates for all solutions. The increase in viscosity level is slow at first and then accelerated. In very dilute solutions, polymer chains interact with each other without forming hydrophobic domains. At a critical micellar concentration, by analogy with low molecular weight surfactants, the hydrophobic ends of polymer start to build flowerlike domains consisting of 10–80 hydrophobes (Pham *et al.*, 1999). As the concentration is increased above another critical level, called the overlap concentration where the micelles begin to overlap and interpenetrate, the micellar bridging occurs and eventually the three-dimensional network of unbounded micelles is developed. At this point, the solution viscosity shows a drastic increase. For HEUR solutions studied, the critical polymer concentration at the onset of association network is estimated to be 0.5 wt% (Horigome *et al.*, 1998).

In solutions of nonassociating linear polymers, the transient network is developed by entanglements above the

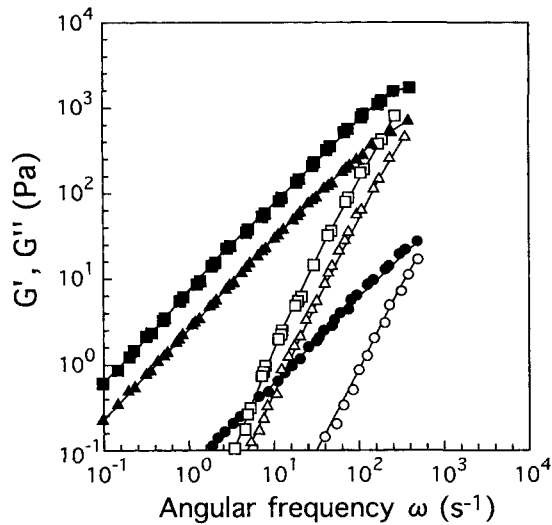


Fig. 2. Frequency dependence of storage (open symbols) and loss (filled symbols) moduli for HEUR solutions at different concentrations: 1.1(○,●); 3.3(△,▲); 5.5 wt%(□,■).

overlap concentration. The concentrated polymer solutions show elastic responses due to the decrease in entropy of polymer chain in the network during extension by shear. Hence, the viscoelastic measurements serve to understand the dynamic structures of associating network. Figure 2 shows the frequency dependence of storage  $G'$  and loss  $G''$  moduli for HEUR solutions at different concentrations. For each solution, the measurements were carried out at various temperatures in the range of 1–25°C and all curves are shifted along the frequency abscissa so as to form a single master curve for a reference temperature. The master curves at the reference temperature of 25°C obtained by superposition are shown in Figure 2. At low frequencies, the storage modulus is correlated by a straight line with a slope of 2, irrespective of polymer concentration. The curves of loss modulus are also superimposed on a line with a slope of 1. The linear viscoelasticity theory predicts that in the terminal region the loss modulus is proportional to the frequency and the storage modulus to the square of frequency. Therefore, the viscoelastic behavior of HEUR solutions in long time scales is characterized by the zero-frequency dynamic viscosity  $\eta_0$  and elasticity coefficient  $A_G$ , where  $\eta_0$  and  $A_G$  are defined by the following equations;

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (1)$$

$$A_G = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2} \quad (2)$$

Supposing that the relaxation process is approximated by a single relaxation model of Maxwell type, the relaxation time can be determined as the ratio of elasticity coefficient

to zero-frequency viscosity.

$$\tau = \frac{A_G}{\eta_0} \quad (3)$$

The relaxation times are estimated to be 0.9, 1.5, and 1.5 ms at HEUS concentrations of 1.1, 3.3, and 5.5 wt%, respectively. One can reach the important conclusion that the lifetime of micellar bridging formed by associating interactions of hydrophobes is of the order of 1 ms.

### 3.2. Stable suspensions

Prior to rheological measurements of suspensions, the sedimentation stability was examined by visual observation at a particle concentration of 10 vol%. The suspensions prepared using polymer solutions at 0.4–1.6 wt% were rapidly separated into clear supernatant solution and opaque solid layers by sedimentation in the quiescent state. The times required for sedimentation were from several minutes to a few hours. The stock suspension without additives is electrostatically stabilized. The sedimentation of particles indicates that the addition of HEUR polymer causes the flocculation of suspensions. Since the HEUR chains can act as stickers of particles, the degree of flocculation is expected to increase with polymer concentration. However, at polymer concentrations of 2.0 wt% and above, the sedimentation was not observed, but the suspensions were very stable. The unique behavior of sedimentation stability implies that the particle-particle interactions and in turn the flocculating power decrease as the polymer concentration is increased above some level. In this section, the rheology of stable suspensions prepared with relatively concentrated solutions will be discussed.

Figure 3 shows the frequency dependence of storage and loss moduli for HEUR solutions and 10vol% suspensions

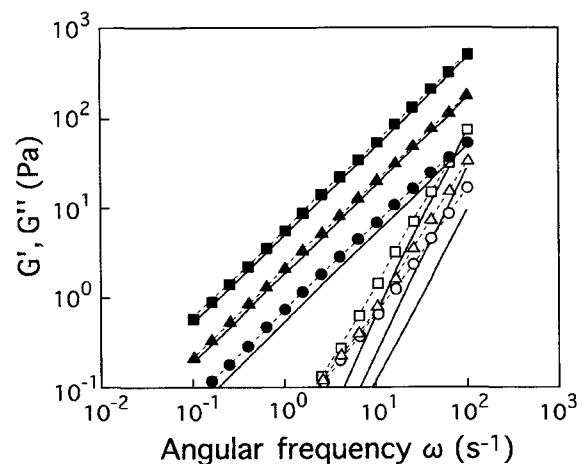
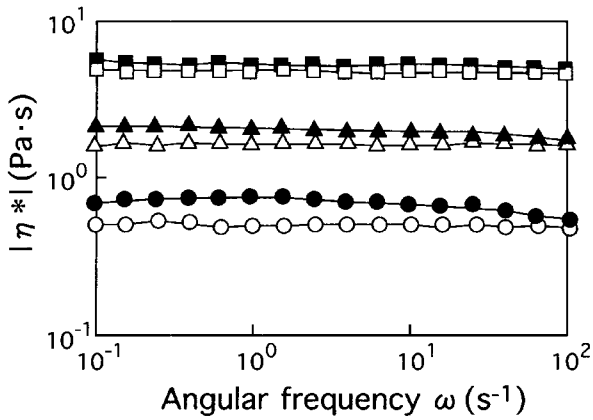


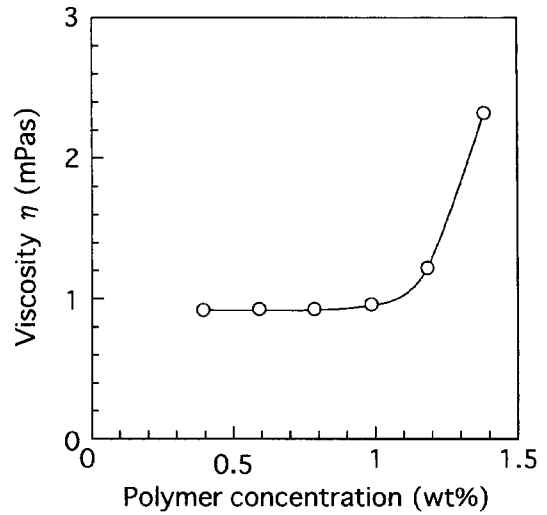
Fig. 3. Frequency dependence of storage (open symbols) and loss (filled symbols) moduli for HEUR solutions (solid lines) and 10 vol% suspensions at different polymer concentrations: 2.0(○,●); 3.0(△,▲); 5.0 wt%(□,■).



**Fig. 4.** Frequency dependence of the absolute value of complex viscosity for HEUR solutions (open symbols) and 10 vol% suspensions (filled symbols) at different polymer concentrations: 2.0(○,●); 3.0(△,▲); 5.0 wt%(□,■).

at different polymer concentrations. In contrast to the quadratic dependence of storage modulus on the angular frequency for HEUR solutions, the plots for suspensions are not correlated by a line with a slope of 2. The discrepancy at low frequencies may be an indication of the existence of flocculated structures. For further discussion, the absolute value of complex viscosity,  $|\eta^*|$  is calculated to evaluate the flocculation level. Figure 4 shows the frequency dependence of  $|\eta^*|$  for HEUR solutions and suspensions. The relative viscosity, defined as the viscosity of the suspension divided by that of the medium is often used as a measure of the degree of flocculation. In many flocculated suspensions, the relative viscosity is reported to be higher than 1000, whereas the value is less than 2.0 for sample suspensions. In addition, the relative viscosity decreases with increasing polymer concentration. The rheological results clearly indicate that the suspensions prepared with relatively concentrated polymer solutions are stable and the flocculation level is very low.

For suspensions which showed the rapid sedimentation, the viscosity of supernatant solutions was measured. The results are shown as a function of polymer concentration in Figure 5. The viscosity of supernatant solutions of suspensions at polymer concentrations below 1.0 wt% is about 1 mPas and almost the same as water. Below 1.0 wt%, all polymer chains are considered to adsorb onto the particle surfaces. Therefore, the adsorbance is determined as 83 mg/g-particles. The suspensions become stable when the polymer concentration is increased beyond 2.0 wt%. If the polymer adsorption reaches the saturation, the polymer concentration in solution phase of stable suspensions would be higher than 1.0 wt%. From Figure 1, the polymer concentration in the medium exceeds the critical value for network formation. By a combination of sedimentation and rheological experiments, the important conclusion is



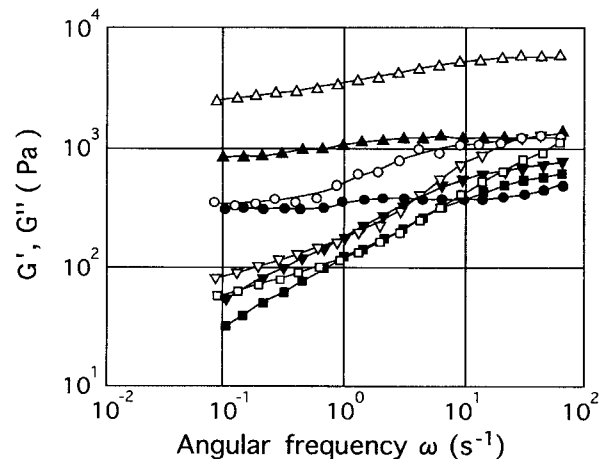
**Fig. 5.** Viscosity plotted against the polymer concentration for supernatant solutions of 10 vol% suspensions.

derived that the particle-particle interactions are very weak and the suspensions are stable against the sedimentation in the conditions where the association network is developed in the solution phase.

### 3.3. Flocculated suspensions

Because of rapid sedimentation, the rheological measurements were difficult for flocculated suspensions at a concentration of 10 vol%. To understand the flocculation mechanism, similar experiments were repeated by the use of 30 vol% suspensions.

Figure 6 shows the frequency dependence of storage and loss moduli for suspensions at different polymer concentrations. It is well known that the storage modulus of



**Fig. 6.** Frequency dependence of storage (open symbols) and loss (filled symbols) moduli for 30 vol% suspensions at different polymer concentrations: 0.3(○,●); 0.5(△,▲); 1.5(□,■), 1.7 wt%(▽,▼).

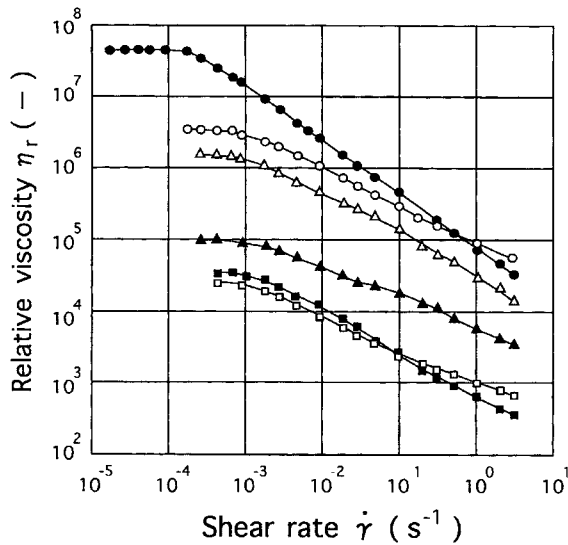


Fig. 7. Shear rate dependence of relative viscosity for 30 vol% suspensions at different polymer concentrations : 0.3(○), 0.5(●), 0.8(△), 1.0(▲), 1.2(□), 1.7 wt%(■).

highly flocculated suspensions shows a plateau at low frequencies. The appearance of plateau can be connected with the development of network structures over the system. However, the clear plateau was not observed for the sample suspensions. Especially above 1.0 wt%, both the moduli rapidly decrease with decreasing frequency. Although an additional relaxation process can be detected as a shoulder in the viscoelastic curves, the energy dissipation in the flocculated structure seems very rapid.

Figure 7 shows the shear rate dependence of relative viscosity for 30 vol% suspensions at different polymer concentrations. As expected from the visual observation of dilute suspensions, the relative viscosity increases at first, passes through a maximum and then decreases as the polymer concentration is increased. The particle-particle interactions are strongly influenced by the polymer concentration. In ordinary flocculated suspensions, the flow becomes plastic with yield stress at very low shear rates when the three-dimensional network of flocs is developed over the system. However, the viscosity of sample suspensions is constant at low shear rates and rapidly decreases with increasing shear rate. The most important feature is that the suspensions flocculated by associating polymers are Newtonian in the limit of zero shear rate and essentially behave as liquids.

In ordinary conditions, polymer adsorption is considered to be irreversible. Since the bridging flocculation is also irreversible, the bridges between particles are not broken down by thermal energy. Hence the suspensions flocculated by irreversible bridging show elastic responses at very low frequencies or plastic responses with infinite relaxation times, when both the particle and polymer concentrations

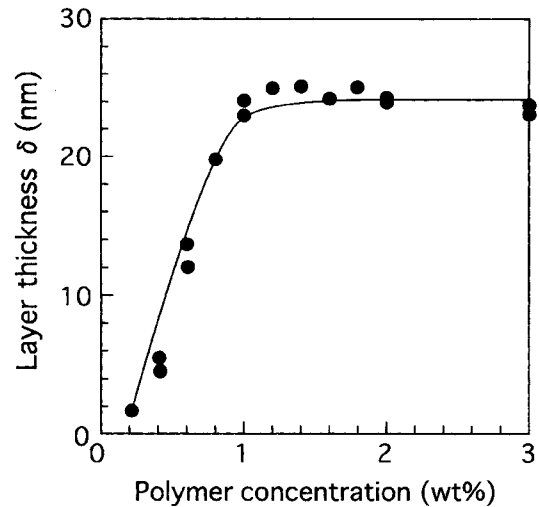
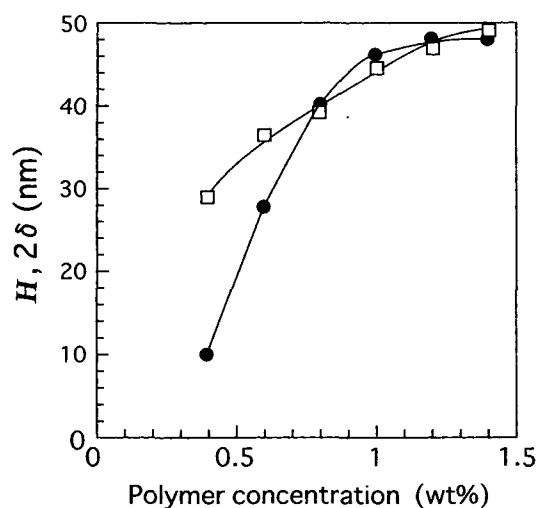


Fig. 8. Thickness of adsorbed polymer layer plotted against the polymer concentration of initial suspensions.

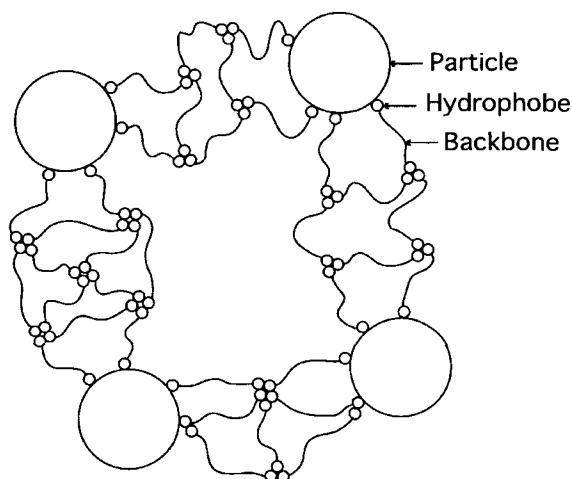
exceed some critical values (Otsubo, 1991). However, the sample suspensions show Newtonian flow at low shear rates. This indicates that the particle-particle bonds formed by polymer bridges are constantly forming and breaking in a quiescent state. Since the associating polymers do not have strong affinity for the particle surface, the adsorption-desorption process reversibly takes place by thermal energy. The intrinsic mechanism of flocculation induced by associating polymers is the reversible bridging.

### 3.4. Bridging conformation

In reversible bridging, the interaction energy between two particles is of the order of  $kT$  (Annable *et al.*, 1993; Pham *et al.*, 1998). The formation and rupture of polymer bridges are constantly repeated in a quiescent state. Therefore, the polymer bridges are very soft and the flocs are easily broken down to individual particles by gentle shear. In fact, the flocculated suspensions were converted to stable systems by the additions of HEUR polymer and the sediments were redispersed by dilution with water. The latter suspensions consist of a collection of non-interacting particles that may be covered with polymer layers. To evaluate the layer thickness, the particle size distribution was measured for dilute suspensions by dynamic light scattering. The average diameters measured were comparable to those of primary particles and the ratio of volume mean diameter to arithmetic mean diameter was 1.06. Presumably the suspensions were highly stabilized and monodisperse states without flocs were established. Figure 8 shows the thickness of adsorbed polymer layer plotted against the polymer concentration of initial suspensions. With increasing polymer concentration, the layer thickness increases and becomes a constant at 1.0 wt%. It is of interest to note that the adsorbance also reaches the saturation as the poly-



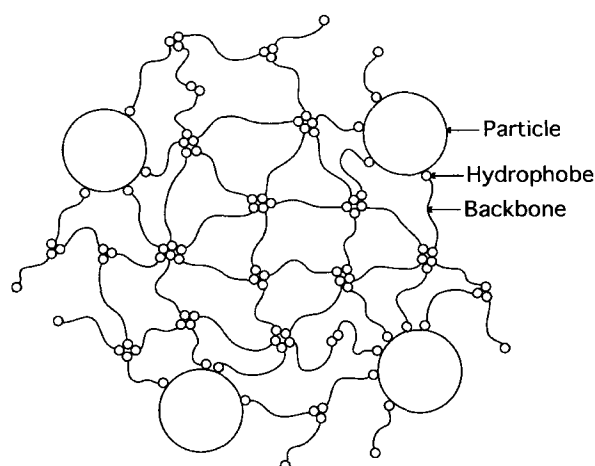
**Fig. 9.** Polymer concentration dependence of surface separation  $H$  (□) in the sediment of 10 vol% suspensions and twice the adsorbed layer  $2\delta$  (●) of isolated particles in dilute suspensions.



**Fig. 10.** A schematic picture of polymer bridging by interchain associations.

mer concentration is increased up to 1.0 wt%. The thickness of adsorbed polymer is about 25 nm under the conditions where the full coverage takes place.

Through the sedimentation experiments, the surface separation is calculated from the mean distance between particle surfaces, on the assumption that the particles are arranged in random sphere packing in the sediments. Figure 9 shows the polymer concentration dependence of surface separation in the sediment of 10 vol% suspensions and twice the adsorbed layer of isolated particles in dilute suspensions. The coincidence of two values above 0.8 wt% implies that even beyond the saturation of polymer adsorption on isolated particles, the bridging occurs when the particles approach to a distance of twice the adsorbed layer. In



**Fig. 11.** A model of suspension structure in which particles are dispersed in the association network.

general, the adsorbed conformation strongly depends on the affinity of polymer for the solid surface. In contrast to ordinary irreversible adsorption, the adsorption process of associating polymers is reversible because of weak affinity for particle surface. As a result, a small amount of polymer chains which are not in direct contact with surface exists in solution. Because such polymer chains can contribute to the particle-particle interactions to bind the particles, the suspensions can be flocculated by multichain bridging. Figure 10 shows a schematic picture of polymer bridging by interchain associations.

When the polymer concentration is increased far beyond the adsorbance at saturation, the drastic decrease in the degree of flocculation is observed through the rheological measurements. In adsorption of non-associating polymers, the excess polymer remains as nonadsorbed coils in the solution phase. The nonadsorbed polymer chains do not significantly contribute to the particle-particle interactions. However, the associating interactions can influence the bridging structure, because the number of polymer chain incorporated in one bridge varies with the polymer concentration. At very low concentrations, the particles are connected by direct adsorption of single chain. The changes from single chain bridging to multichain bridging with increasing polymer concentration have been discussed in a previous paper (Hogigome and Otsubo, 2002). In addition, the flowerlike micelles and three-dimensional network, which result in high viscosity, can be created in solution phase at high concentrations. The suspension rheology is controlled by a balance between the particle-particle interactions and hydrodynamic forces which are related to the solution viscosity. The multichain bridges may be flexible and the strength is low at high polymer concentrations. Since the hydrodynamic forces become predominant, the relative viscosity decreases with increas-

ing polymer concentration. Figure 11 shows a model of suspension structure in which particles are dispersed in the association network. The presence of particles does not influence the associating network and therefore the suspension rheology is described by polymer rheology.

#### 4. Conclusions

The addition of small amounts of associating polymer causes flocculation of colloidal suspensions by reversible bridging. The degree of flocculation increases at first, passes through a maximum and then decreases as the polymer concentration is increased. In suspensions prepared using polymer solutions at 0.4~1.6 wt%, the polymer chains effectively form bridges between particles by multichain association. When the polymer concentration is increased above the adsorbance at saturation, the excess polymer chains remaining in the solution phase build up three-dimensional network by associating interactions. The relative viscosity of suspensions is drastically decreased with increasing polymer concentrations. In the medium in which association network is developed, the particle-particle attraction is very weak and the systems are dispersed to a great extent. The bridging conformation and flocculation level vary strongly depending on the polymer concentrations.

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