Colloid Polym Sci (2008) 286:1537–1544
DOI 10.1007/s00396-008-1928-5

ORIGINAL CONTRIBUTION

Rheological behavior of silica suspensions in aqueous solutions of associating polymer

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Received: 4 July 2008 / Revised: 27 August 2008 / Accepted: 30 August 2008 / Published online: 13 September 2008

Abstract Associating polymers are hydrophilic long-chain molecules containing a small amount of hydrophobic groups. The aqueous solutions show viscoelastic responses above some critical concentrations because a three-dimensional structure is formed by association of hydrophobic groups. When the associating polymers are added to silica suspensions at low concentrations, the flocculation is induced by bridging mechanisms, and the flow of suspensions become shear-thinning. For suspensions prepared with polymer solutions in which the associating network is developed, the viscosity decreases, shows a minimum, and then increases with increasing particle concentration. The viscosity decrease may arise from the breakdown of associating network due to adsorption of polymer chains onto the silica surfaces. As the particle concentration is increased, the polymer concentration in solution is decreased, and finally, all polymer chains are adsorbed on the surfaces. Beyond this point, the partial coverage of particle surfaces takes place and strong interactions are generated between particles by polymer bridging. Since the stable suspensions are converted to highly flocculated systems, the viscosity is increased and the flow becomes shear-thinning. The concentration effect of silica particles on the viscosity behavior of suspensions can be explained by a combination of viscosity decrease in solution due to polymer adsorption and viscosity increase due to flocculation.

Keywords Associating polymer · Bridging flocculation · Shear thinning · Suspension · Viscosity

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Introduction

Water-soluble long chains carrying a small fraction of hydrophobic groups (hydrophobes) are known as associating polymers. In aqueous solution, the hydrophobes can aggregate by associating interactions in the same manner as surfactant molecules form micelles. The associating polymers in which the hydrophobes are incorporated as terminal groups form flowerlike micelles beyond a critical micellar concentration [1–3]. When the polymer concentration is increased, two flowerlike micelles are connected by bridging, and eventually, a three-dimensional structure of transient network is constructed over the system. Due to interchain associations, the aqueous solutions of associating polymers exhibit unique rheological properties including shear-thickening flow and high elasticity at large strains [4–9]. The associating polymers can give rise to high viscosity with Newtonian flow profiles over a wide range of shear rates for water-borne latex suspensions, in contrast to traditional thickeners such as cellulose polymers. Therefore, they have received increasing interests as thickeners for paints and coatings [10–13]. For accurate control of suspension rheology in application to coating and printing technology, it is essential to understand the adsorption behavior of polymer onto particle surfaces and resultant interactions between particles [10, 14, 15].

Since the hydrophobes can adsorb onto the hydrophobic surfaces, the associating polymers act as flocculants in latex suspensions, and their effects on suspension rheology are extensively studied by various authors [16–20]. In previous papers [21–23], we have studied the rheological properties of latex suspensions flocculated by bridging of associating polymers. From a fact that the rheological values such as viscosity, elasticity, and relaxation time are not given by a simple function of polymer concentration, two bridging models are proposed. One is the direct bridging of a single chain in which two hydrophobes are adsorbed onto different particles to bind them together. The other is the multichain bridging in which the particles are connected by linkage of interchain associations. The mechanical properties of a bridge as a unit bond are strongly affected by the particle and polymer concentrations.

The adsorption conformation of associating polymer and flocculation mechanisms vary depending on the surface chemistry of the particles [24]. We have also studied the viscosity behavior of silica suspensions in the presence of associating polymers [25]. In the adsorption of associating polymers onto silica particles, the chain adopts a conformation with the water-soluble backbone attached to the particle surfaces. The flocculation can be induced by association interactions of hydrophobes extending from the chains adsorbed onto different particles. As a result, the suspensions show high viscosity with shear-thinning profiles. The addition of surfactant to silica suspensions flocculated by associating polymer causes a viscosity increase. This can be attributed to the enhancement of particle–particle bonds by association with surfactant molecules.

Both hydrophilic and hydrophobic particles are flocculated by associating polymer, and the flow of suspensions becomes shear-thinning. In many cases, the primarily responsible factors controlling the suspension rheology are the flocculated structures and, in turn, the particle–particle interactions. But in aqueous solutions of associating polymers, the micellar bridging between polymer chains through association of hydrophobes strongly influences the solution viscosity. Therefore, the rheological properties of suspensions in solutions of associating polymers are determined by a dynamic equilibrium between hydrophobe adsorption onto particle surfaces and hydrophobe association in the suspension medium. In the present paper, the polymer adsorption and rheology are studied for suspensions of silica particles dispersed in associating polymer solutions. The attention is focused to the relation between floc formation of particles and network formation of polymer chains.

Materials and methods

Materials

The suspensions were composed of silica, associating polymer, and water. The silica particles (Silica Micro Bead P-500) were manufactured by Catalysts and Chemicals Industries (Japan), the diameter and density of which were 1.3 μm and 2.1×10^3 kg m^{-3}, respectively. The degree of polydispersity which is given as the ratio of standard deviation to the average diameter was 0.25. The associating polymer was hydrophobically modified ethoxylated urethane (HEUR; RM-825 from Rohm and Haas), the molecular weight of which was about 25,000. The hydrophobes are incorporated on the ends of molecule as terminal groups. The suspensions were prepared at particle concentrations up to 30% by weight. The polymer concentration was in the range of 0–2.0% by weight based on the water. The rheological measurements were carried out after the suspensions were stored at room temperature under gentle shear on a rolling device for about 2 h.

Methods

Shear rate dependence of viscosity was measured using a coaxial cylinder geometry on a stress-controlled rheometer (Haake Rheo-Stress RS75). The diameters of the bob and cup were 20 and 22 mm, respectively. The immersion length of bob was 30 mm. The viscosity measurements were carried out in the procedure that the shear rate was stepwise increased and decreased in the range of 0.3 and 300 s^{-1} in a measuring time of 30 s at each shear rate. The total measuring time for one sample was about 20 min. Significant differences were not observed between the up-curve and down-curve. Neither sedimentation of particles nor time dependence such as thixotropy was detected in the timescale of viscosity measurements. The measuring temperature was 25 °C for all runs.

Prior to the systematic rheological measurements, the effect of wall slip was examined because highly flocculated suspensions often cause slip at solid boundaries in rheometers. The errors due to wall slip can be corrected by a technique proposed by Yoshimura and Prud'homme [26]. Their technique involves two measurements on a parallel plate geometry with different gap settings. In this study, the shear rate dependence of viscosity was measured in parallel plate and coaxial cylinder geometries for suspension with the highest viscosity at low shear rates. A slight wall slip was observed, which could result in an error of about 40% in viscosity values at low shear rates less than 1 s^{-1}. Thus, the results at shear rates where the wall slip was not detected are presented.

Adsorption of polymer on the particle surface was determined by the sedimentation experiments. To calculate the concentration of non-adsorbed polymer, the particles or flocs were separated by centrifugation at 3,000×*g* for 1 h and by gravitational sedimentation at rest for more than 24 h. The amounts of polymer adsorbed on the particles were calculated from the residual polymer concentrations which were determined through the viscosity measurements. The particle separation was carried out under different conditions, but the adsorbance of polymer was not influenced by the sedimentation procedures.

The destabilization process of suspensions was monitored by the use of an optical instrument (Turbican manufactured by Formul Action) which was developed for evaluation of colloidal stability.

This technology is based on multiple light scattering concept. In a dense scattering medium, the incident light undergoes several scattering events before transmission through the sample or backscattering. On the basis of the diffusion approximation, the characteristic lengths involved in multiple light scattering phenomena can be related to the physical features of disperse system (mean diameter and particle volume fraction). The detection head which moves up and down along a test tube uses LED emitting in the near infrared (850 nm), transmission light detector, and backscattering light detector located at 135° from the incident light direction. The Turbiscan allows the characterization of suspensions in a wide range of particle volume fraction (0% to 60%) and particle diameter (0.01 to 1,000 mm). In the present study, during the gravitational sedimentation at rest, the light scattering properties of suspensions were measured as a function of time by scanning the entire length of the sample in a test tube. The time dependence of intensity profile can be connected with the size changes due to flocculation and concentration changes due to sedimentation [27, 28].

Results and discussion

Suspension rheology and polymer adsorption behavior

Figure 1 shows the shear rate dependence of viscosity for 30 wt.% suspensions in HEUR solutions at different concentrations. The suspension consisting of silica particles and water is Newtonian with viscosity of 2.2 mPa s. The addition of associating polymer leads to a striking increase in viscosity, and the overall flow profile becomes shear-thinning. The shear-thinning flow of suspensions is often explained by the progressive breakdown of flocculated structures in shear fields. The suspensions may be highly flocculated in the presence of associating polymer. The viscosity increases with increasing polymer concentration and looks likely to approach a constant level above 1.0 wt.%.

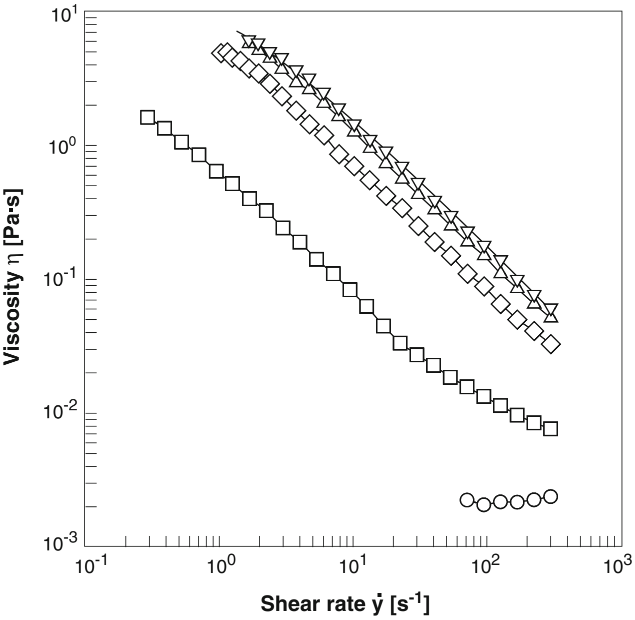

Fig. 1 Shear rate dependence of viscosity for 30 wt.% suspensions at different polymer concentrations: 0 (*circle*); 0.5 (*square*); 1.0 (*diamond*); 1.5 (*triangle*); 2.0 wt.% (*inverted triangle*)

Figure 2 shows the shear rate dependence of viscosity for 20 wt.% suspensions in HEUR solutions at different concentrations. The viscosity of suspensions is remarkably increased by associating polymer. The flocculating ability of associating polymer is regarded as considerably high. In many suspensions flocculated by non-associating polymers, the viscosity as a manifestation of degree of flocculation increases with increasing polymer concentration and reaches the saturation. However, the viscosity level of sample suspensions increases, shows a maximum, and decreases as the polymer concentration is increased. The effect of associating polymer on the viscosity behavior of silica suspensions is very complicated. This implies that the colloidal interactions between two particles vary depending on the polymer concentration.

Figure 3 shows the effect of particle concentration on the viscosity behavior of suspensions prepared with a 2.0 wt.%

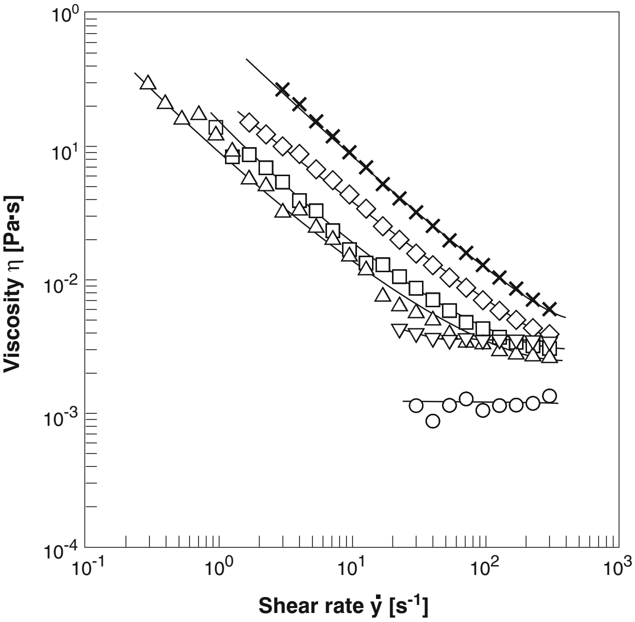

Fig. 2 Shear rate dependence of viscosity for 20wt% suspensions at different polymer concentrations: 0 (*circle*); 0.5 (*square*); 0.75 (*ex*); 1.0 (*diamond*); 1.5 (*triangle*); 2.0 wt.% (*inverted triangle*)

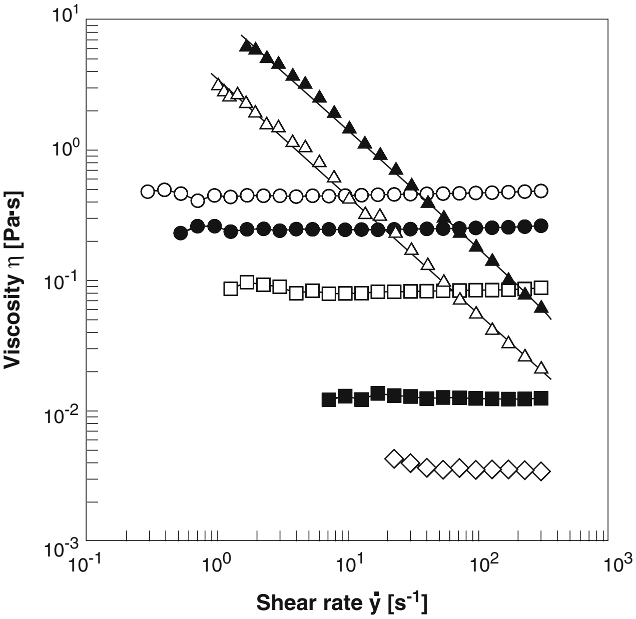

Fig. 3 Effect of particle concentration on the viscosity behavior for suspensions in a 2.0 wt.% HEUR solution: 0 (*open circle*); 5 (*filled circle*); 10 (*open square*); 15 (*filled square*); 20 (*diamond*); 25 (*triangle*); 30 wt.% (*filled triangle*)

HEUR solution. The medium and suspensions up to 20 wt.% are Newtonian over the entire range of shear rates studied, while more concentrated suspensions are strikingly shear-thinning. There exists a critical particle concentration where the sudden change of flow profile occurs. With increasing particle concentration, the viscosity decreases, shows a minimum, and then increases. It must be stressed that the Newtonian viscosity for suspensions at particle concentrations below 20 wt.% is lower than that of medium. Generally, the increase in particle concentration gives rise to the enhancement of suspension viscosity if the particle–particle interactions were independent of concentration. According to Einstein theory of suspension rheology for non-interacting particles, the increase in viscosity is attributed to the distortion of the velocity field in the vicinity of each particle. The addition of particles inevitably causes a viscosity increase of the liquid. It seems difficult to explain the reduction of suspension viscosity by the previously established mechanisms such as hydrodynamic interactions and floc formation by colloidal forces.

The flow profiles of silica suspensions in aqueous solutions of associating polymer drastically change from Newtonian to shear-thinning at some particle concentrations. A diagram showing the regions of different flow profiles is given in Fig. 4. The Newtonian flow is observed for suspensions at low particle concentrations prepared with solutions at relatively high polymer concentrations. The adsorbance of associating polymer on the silica particles was determined to be about 77 mg/g particles from the viscosity measurement of supernatant solutions. For instance, this value corresponds to about 1.9 wt.% polymer in 20 wt.% suspensions. Therefore, all polymer chains may be adsorbed on the particle surfaces in the suspensions at higher particle concentrations or those prepared with solutions at lower polymer concentrations. The solid line in Fig. 4 shows the boundary at which the full coverage of particle surfaces with polymer takes place. In suspensions with compositions below the boundary line, non-adsorbing polymer chains remain in solution phase. It is of interest to note that the transition from Newtonian to shear-thinning profiles occurs in the vicinity of this boundary line. The suspensions under the full coverage conditions are Newtonian, whereas those under partial coverage conditions are shear-thinning.

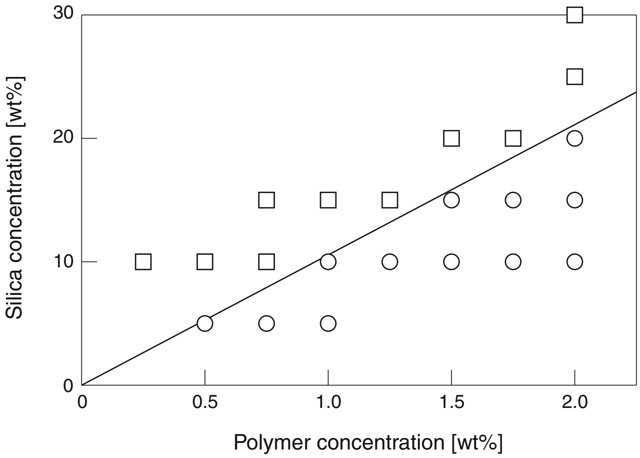

Fig. 4 A diagram showing the regions of different flow profiles: Newtonian flow (*circle*); shear-thinning flow (*square*); saturation coverage boundary (*solid line*)

For a better understanding of the flow mechanism of Newtonian systems, the comparison of viscosity between suspensions and their supernatant solutions is summarized in Fig. 5. In contrast to ordinary suspensions, the viscosity decreases with increasing particle concentration. The concentration-dependent curves of viscosity for suspensions and supernatant solutions are very similar, indicating that the primary factor controlling the suspension viscosity is the viscosity of the medium. The viscosity for suspension of non-interacting spherical particles can be calculated through Einstein theory. For example, the particle concentration of 20 wt.% in sample suspensions corresponds to 10.5 vol.%, and the relative viscosity which is defined as the viscosity of the suspension divided by that of the medium is estimated to be 1.26. The values experimentally obtained at polymer concentrations of 2.0 wt.% is about 4.4. The relative viscosity is slightly higher than the theoretical prediction for non-interacting particles. The weak interactions between particles may contribute to the increase in suspension viscosity. However, this effect is relatively weak compared

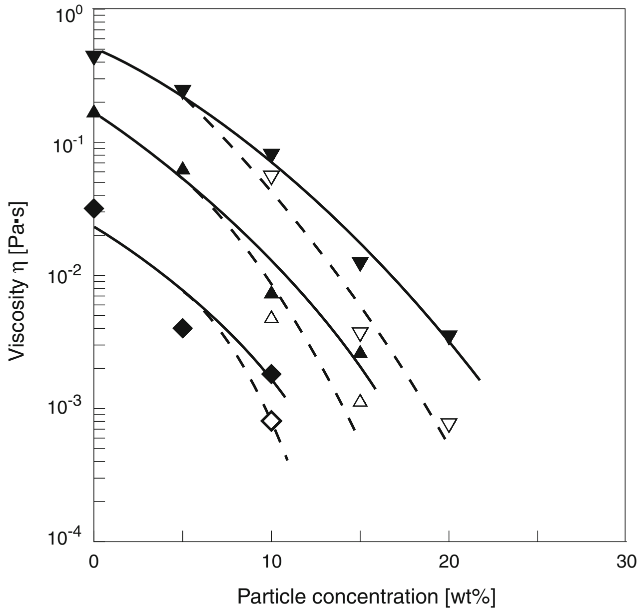

Fig. 5 Particle concentration dependence of viscosity for Newtonian suspensions (*filled symbols*) and their supernatant solutions (*open symbols*) prepared with HEUR solutions at different concentrations: 1.0 (*open diamond*, *filled diamond*); 1.5 (*open triangle*, *filled triangle*); 2.0 wt.% (*inverted triangle*, *filled inverted triangle*)

with hydrodynamic forces from the medium. Therefore, the suspensions in which the full coverage of particle surfaces with polymer takes place are regarded as well-dispersed systems.

Relation between sedimentation behavior and bridging conformation

The suspensions in which the adsorbance of polymer chain does not reach the saturation, but the partial coverage of particle surfaces takes place, are shear-thinning. The viscosity change induced by polymer may directly reflect the change in the flocculation structures of silica particles. To provide more insight into the particle–particle interactions and flocculation structure, the sedimentation behavior is optically analyzed. In the present study, the intensities of lights transmitted across the sample and scattered backward by the sample were simultaneously monitored for 24 h by vertically scanning the test tube with an accuracy of 40 µm.

Figure 6a,b shows the height dependence of transmission and backscattering intensities, respectively, in percent relative to the initial stage right after the sample preparation for 10 wt.% suspension in a 0.5 wt.% HEUR solution. Because of limitation of instruments and experimental conditions, both intensities are given in the range of about −30% to 60%. The transmission intensity shows a rapid increase at heights of about 60 mm. The top region with high transmission is almost transparent and is expanded with time. The sharp change in transmission intensity corresponds to the boundary between turbid suspension and supernatant liquid. This effect is due to clarification, and the particles may be concentrated in suspension phase below the settling front. In suspensions, the increase in particle concentration can be observed as an increase in backscattering intensity, even though the change of transmission is not detected. Therefore, the backscattering intensity is expected to increase in the whole region of turbid layer during sedimentation. However, another boundary can be seen at heights of 5–15 mm, below which the sediment with higher particle concentrations is formed and above the dilution proceeds by settling. The suspension phase consists of two layers with different particle concentrations.

Figure 7a,b shows the height dependence of transmission and backscattering intensities, respectively, for 10 wt.% suspension in a 1.0 wt.% HEUR solution. From the transmission curves, the height of boundary line between turbid suspension and supernatant liquid rapidly decreases with time. In addition, the sediment is rapidly formed at the bottom of suspension phase. The transmission shows a sharp increase at heights where the backscattering begins to decrease in the upper part of turbid suspensions. Because the particle concentration in the intermediate turbid layer is kept constant, the concentration reduction in supernatant solution and the concentration increase in the sediments should balance each other. The most interesting feature is that the sedimentation process is completed in 3 h and the final system consists of solid-like sediment and transparent supernatant liquid, whereas the suspension prepared with

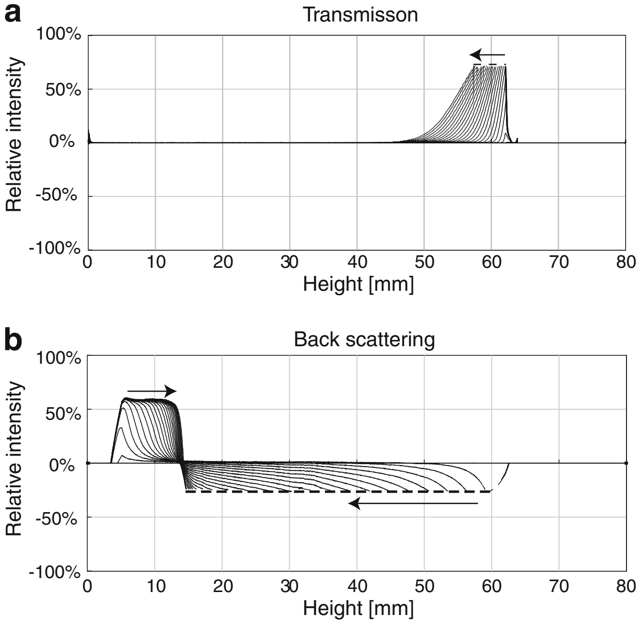

Fig. 6 Height dependence of transmission (**a**) and backscattering intensities (**b**) for 10 wt.% suspension in a 0.5 wt.% HEUR solution at different sedimentation periods: 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, and 24 h in the direction of *arrow*

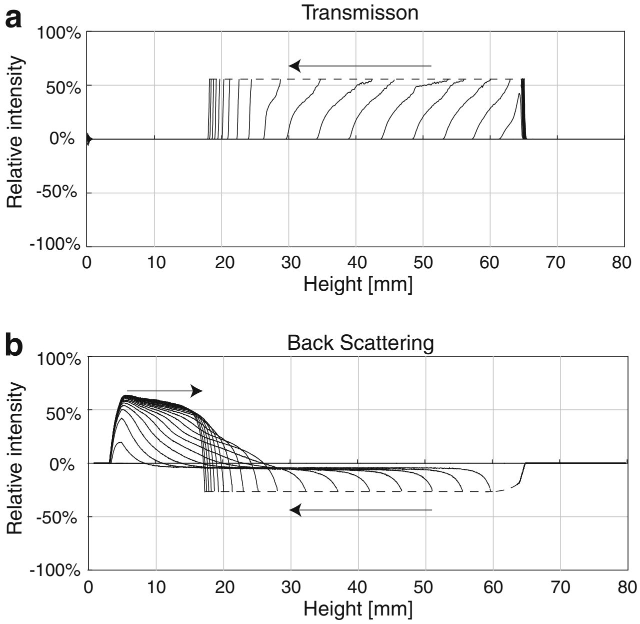

Fig. 7 Height dependence oftransmission (**a**) and backscattering intensities (**b**) for 10 wt.% suspension in a 1.0 wt.% HEUR solution at different sedimentation periods: 0, 0:10, 0:20, 0:30, 0:40, 0:50, 1 h, 1:10, 1:20, 1:30, 1:40, 1:50, 2 h, 2:10, 2:20, 2:30, 2:40, 2:50, and 3 h in the direction of *arrow*

0.5 wt.% HEUR solution consists of three layers even after the sedimentation period of 24 h.

For 10 wt.% suspension in a 2.0 wt.% HEUR solution, it is confirmed that the transmission is kept constant and independent of time. The backscattering shows a very little change near the surface (about 2 mm in depth). The suspensions containing sufficient HEUR beyond the full coverage exhibit very high stability against sedimentation.

The additions of small amounts of associating polymer cause the viscosity increase of silica suspensions. The intrinsic mechanism is the flocculation by polymer bridging. When the non-associating polymers such as polyethylene glycol are added to silica suspensions, the viscosity is increased to a great extent and flow becomes shear-thinning in a wide range of shear rates. The similar effects of polymers on the suspension rheology imply that under the condition of partial coverage, the hydrophobes at the ends of associating polymers do not significantly influence the bridging conformation. In adsorption of non-associating polymer on the silica surfaces, not all the segments of a polymer coil are in contact with the surface, but each polymer chain is attached in sequence separated by segments which extend into solution. Since the long loops extending from particles with adsorbed layers come into contact with surface of bare particles, flocculation occurs by a bridging mechanism [29, 30]. In general, polymer adsorption is essentially irreversible because the polymer chain may attach to the surface at several points and may not be able to desorb simultaneously from all sites. The bridges between particles are not broken in a quiescent state, but progressively broken in shear fields. As a result, the flow of flocculated suspensions is shear-thinning. The shear-thinning profiles observed for suspension containing HEUR at low concentrations can be explained by the irreversible bridging. In the limit of zero shear rates, the sedimentation processes are very slow due to the geometrical hindrance of large flocs developed over the system. When the particles are fully covered with thick layers of adsorbed polymer, the suspensions are often stabilized by steric effects of polymer chains. Slightly below the full coverage, the suspensions consist of large flocs and isolated particles. Hence, the three layers are formed in a test tube during sedimentation experiments.

The suspensions containing HEUR at concentrations slightly above the full coverage show Newtonian flow with low viscosity. This is a typical flow profile for suspensions in highly dispersed states. But the sedimentation rate is very high, indicating the existence of flocs. In these suspensions, the excess polymer chains can remain as non-adsorbed coils in solution phase. Although the adsorption sites on the silica surfaces may be fully occupied by segments of hydrophilic backbone, the chain adopts a conformation with the hydrophobes extending into solution. The dangling ends of the adsorbed chain can make aggregation by associating interactions with hydrophobes of non-adsorbed chains. Thus, the particles can be connected by the multichain bridging. Because of weak associating interactions, the particle–particle bonds are forming, breaking, and reforming by thermal energy. Since the dynamic structures of flocs are not influenced by shear rate, the flow is Newtonian. In the absence of shear fields, the cooperative rearrangements of particles can occur in flocs. Presumably, all particles are collected in huge flocs, and hence, the sedimentation rate is strikingly increased. The weak and reversible bridging may be responsible for Newtonian flow and rapid sedimentation.

The suspensions containing sufficient HEUR beyond the full coverage show Newtonian flow and high stability against sedimentation. In concentrated HEUR solutions, the association of hydrophobes causes micellar bridging and eventually results in the formation of three-dimensional network of unbounded micelles. The viscosity slowly increases at first and the increase is accelerated [31]. From the viscosity behavior, the critical polymer concentration at the onset of association network is estimated to be 0.7 wt.% [25]. Because the polymer concentration in supernatant solution for 10 wt.% suspension in a 2.0 wt.% HEUR solution was 1.12 wt.% from centrifugation experiments, the association network can be developed over the system.

The suspensions containing sufficient HEUR beyond the network formation boundary show Newtonian flow and high stability against sedimentation. Because the association network can be developed over the system, the medium is regarded as a viscoelastic liquid. The high stability against sedimentation is attributed to the formation of transient network by association interactions of hydrophobes in continuous medium. Figure 8 shows the bridging models to understand the change in the particle–particle interactions with polymer concentration. The bridging conformation can be of three types: (a) irreversible bridging at low polymer concentrations, (b) weak reversible bridging slightly above the saturation coverage, and (c) stabilized particles in the associating network of polymer.

Now consider the concentration dependence of suspension viscosity. The viscosity of silica suspensions in HEUE solutions is governed by three factors: volumetric effect of primary particles, floc formation, and adsorption of polymer on the particle surfaces. When the silica particles are dispersed at low concentrations in HEUR solutions whose concentration is beyond the critical value for formation of association network, the viscosity of the solution is drastically decreased by the breakdown of associating network. The suspensions of nanoparticles dispersed in solutions of non-associating polymers often show the viscosity reduction [32, 33]. The gross molecular structure is represented by a flexible coil with a radius of gyration which is much larger than nanoparticles. Many particles can be connected by one polymer chain with coil conformation. The decrease in polymer coils by intrachain bridging can cause the viscosity reduction. But the silica particles are of the order of millimeters. The coil size reduction is not acceptable as a mechanism for explanation of the results. The viscosity decrease observed in the present study may be coupled by reduction of network density due to adsorption of polymer onto the particle surfaces. Under the conditions where the particle surfaces are fully covered with adsorbed polymer, the colloidal interactions between particles are very weak. Since the viscosity decrease of solution dominates the volumetric effect of particles, the viscosity of suspensions decreases with increasing particle concentration. The increase in particle concentration brings about the decrease in the polymer concentration, and finally, all polymer chains are adsorbed onto the particle surfaces. At this concentration, the minimum viscosity is achieved. Further additions of particles lead to the changes in conformation of adsorbed chains. Because the system does not have sufficient chains for full coverage of particle surfaces, the strong interactions are generated between particles by polymer bridging. Therefore, the viscosity is increased and the profile becomes shear-thinning. The effects of particle concentration on the viscosity behavior of suspensions prepared with HUER solutions in which the association network is developed can be explained by a combination of viscosity decrease in solution due to polymer adsorption and viscosity increase due to flocculation.

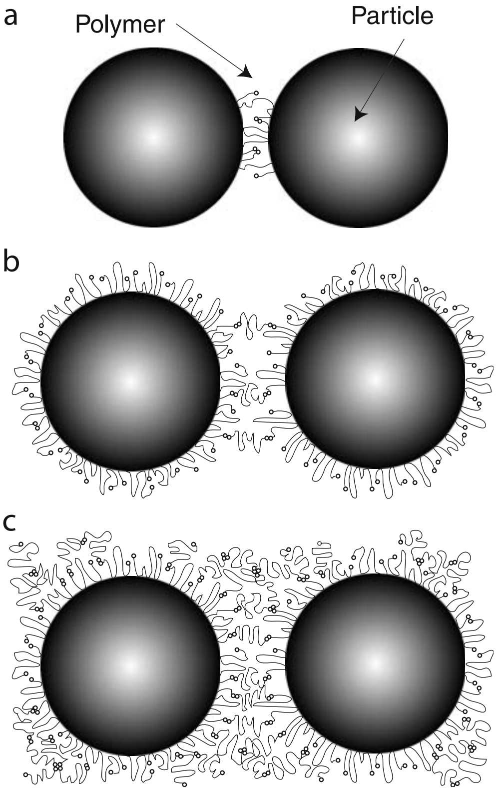

Fig. 8 Conformation models of bridging flocculation induced by associating polymer: **a** irreversible bridging at low polymer concentrations; **b** weak reversible bridging slightly above the saturation coverage; **c** stabilized particles in the associating network of polymer

As far as the rheology control of suspension is concerned, the most important aspect is that the flow profile of suspensions shows a drastic change from Newtonian to shear-thinning at some particle concentrations. The flocculated structures in ordinary suspensions are not broken down by thermal energy. The application of shear fields gives rise to rupture of structures. It is generally accepted for the flow curves of flocculated suspensions that with increasing degree of flocculation, the viscosity increases and the shear-thinning tendency becomes striking. In suspensions flocculated by associating polymers, the particle–particle interactions vary depending on the balance between the particle and polymer concentrations. The associating polymers can cause the changes in viscosity level and flow profile of suspensions. Therefore, this technique has great potential to formulate the suspensions in which the viscosity level and flow profile are independently controlled.

Conclusions

The associating polymers form a three-dimensional structure of transient network by association of hydrophobes above some critical concentrations. When the silica particles are dispersed in such polymer solutions, the viscosity decreases, passes through a minimum, and then increases with increasing particle concentration. The reduction of network density due to adsorption of polymer onto the particle surfaces is primarily responsible for viscosity decrease in suspensions. As the particle concentration is increased, the polymer concentration in solution is decreased, and finally, all polymer chains are adsorbed on the surfaces. Beyond this point, the strong interactions between particles are generated by polymer bridging. The shear-thinning profiles can be attributed to the flocculation of particles. The particle concentration influences the viscosity behavior in two opposing ways, depending on the HEUR concentration.

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