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I. INTRODUCTION

Polymers are invariably used in the processing of ceramic systems for dispersion of suspensions or controlled aggregation. While adsorption density of the polymer on the particles is an important criterion in this regard, equally important is the conformation and orientation of the adsorbed polymer. In this chapter, methods to monitor the conformation and orientation of polymers on particles in situ are described along with the effect of variables such as solids concentration that are clearly relevant in ceramic systems. Desired dispersion/aggregation of particles can be obtained in ceramic systems by first establishing the optimal conformation of the adsorbed species for the given purpose.

There currently exists no clear and universally-accepted definition of the term 'concentrated suspension'. The meaning of the term, therefore, is quite often user-dependent and may vary widely across different industries. Suspensions may be considered to fall between two extremes: dilute suspensions and solids. Firstly, dilute suspensions can be thought of as suspensions in which the thermally-driven Brownian motion of the particles outweighs any effects arising as a result of inter-
particle forces [1,2]. In such suspensions, the constituent particles do not 'see' each other and thus move independently except for the occasional chance collision between them. Two-body interactions between pairs of particles can therefore be used to describe their colloidal properties. At the other extreme is the 'ordered' or 'solid' suspension in which particles occupy specific sites with respect to one another. 'Concentrated suspensions' is loosely applied to any suspension system falling in between the above extremes. These are often the systems of greatest practical interest to industry. Compared to the 'dilute' suspensions, the particles in these systems 'see' and 'feel' each other within relatively short time scales and their interactions are many-body in nature such that their translational motion is restricted [3]. The properties of such systems are complex, often exhibiting spatial and temporal dependencies, making it virtually impossible to theoretically model the microstructure to any great degree of accuracy. Hence, the ability to relate particle properties to macroscopic suspension properties like stability and rheology in practical applications is typically nonexistent.

Industrially, therefore, an empirical approach is often taken regarding the control of concentrated suspension properties. The addition of surfactants and polymers to such suspensions to achieve the desired stabilization, flocculation or rheology enjoys an increasing amount of attention as a result of its applicability in fields ranging from water treatment and minerals and materials to food processing and cosmetics and pharmaceutical production [4,5,6]. Such additives are used in preference—or in addition—to other chemicals like salts and acids/alkalis because the stability of these suspensions is often controlled by several other forces in addition to the electrostatic force [7]. For example, it is important to recognize that suspension stabilization can result from steric repulsion or short-range solvation forces [8,9], and that bridging by adsorbed polymers is an acceptable complement to charge neutralization for achieving flocculation [10].

The stabilization/flocculation provided by adsorbed layers of surfactants and polymers is known to depend, in addition to surface charge, on the conformation and orientation of these molecules at the particle-solution interface and on the microstructure of the adsorbed layer, all of which contribute to the steric and bridging interactions between particles [10,11,12]. While there have been some studies on the behavior of concentrated suspensions per se [1-3,13-28], there have been virtually none dealing with the specific issues of polymer/surfactant conformation/orientation as they relate to suspension properties. A review of the difficulties in characterizing concentrated suspensions is available [29], but even there little mention is made of the role of the adsorbed layer microstructure in affecting the suspension properties. The microstructure of such adsorbed layers has been studied in detail by several groups and correlated with dispersion properties like stability/flocculation, wettability and hydrophobicity of the particles in aqueous [10-30] and nonaqueous [31-35] media. Mainly, it has been difficult to monitor the conformation of adsorbed layers in situ in concentrated suspensions due to lack of suitable techniques. Recently, monitoring of the adsorbed layer has been facilitated, for the most part, by the use of several spectroscopic techniques [10-12,30-
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42], like fluorescence, electron spin resonance (ESR), nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopy. While this work has lead to significant advances in understanding the relationships between adsorbed polymer and surfactant orientation, conformation and organization and some dispersion properties, it has to be stressed here that these studies all apply to dilute suspensions only. Here a brief overview of our recent efforts in monitoring the conformation and orientation of adsorbed polymers in concentrated suspensions is discussed, along with the preliminary results correlating the adsorbed layer microstructure to the observed suspension behavior.

II. POLYMER ADSORPTION AND CONFORMATION

A knowledge of polymer adsorption and conformation at solid-solution interfaces under various conditions can help to develop an understanding of how they function as stabilizers and flocculants. This topic has been the focus of significant theoretical effort since the 1950s and several extensive reviews are available [43-47]. Here a brief summary of some of the available theories is given.

Polymer adsorption is a complex process governed by polymer-surface, polymer-solvent and polymer-polymer interactions. In addition to the amount adsorbed, conformation of the adsorbed species must also be considered while trying to analyze dispersion properties. Typical polymer adsorption densities would correspond to layers more than ten polymer molecules thick if all segments were to be treated as being in contact with the surface [48]. Polymers have thus been suggested to adsorb such that only some of the segments maintain contact with the surface. Those segments in direct contact with the surface are called “trains”, those in between trains but extending into solution are called “loops”, and the free ends of the polymer extending into solution are called “tails”. The distribution of these different segments then represents a measure of both the adsorption and conformation of the polymer molecule.

A. Theory

From a theoretical point of view, several models have been proposed. An overview of these may be found in a recent monograph [49]. One early model has been that put forward by Scheutjens and Fleer [49-51], the numerical self-consistent-field (SCF) model. In this approach the polymer chains are individually represented as step-weighted walks on a two dimensional or three dimensional lattice for the surface and solution, respectively. The equations governing the statistical weights of these walks can be solved numerically, and in so doing, it is possible to obtain information on the polymer chain statistics in addition to the concentration profile. For example, it is possible to determine the probability that a polymer segment a distance z from the surface belongs to either a loop or a tail. This mean-field approach is able to describe a wide variety of adsorbed polymer layers. It is,
however, prone to the disadvantage of difficulty in recognizing general trends (e.g., dependence of layer thickness on segmental adsorption energy).

At the same time, different approaches specifically designed to interpret just such trends have been developed, perhaps the most well-known being that proposed by de Gennes [52]. His proposed scaling analysis argues that under plateau adsorption conditions the adsorbed layer ought to be characterized by a correlation length of concentration fluctuations, $\xi$, proportional to a power of the local concentration, $\phi$: $\xi \propto \phi^{\alpha}$. The exponent $\alpha$ would be unity in a theta solvent and smaller in good solvents. In the absence of other length scales, $\xi$ can be seen to be proportional to the distance $z$ from the wall, and the local concentration then falling off by the power law $\xi \propto z^{-1/\alpha}$. This power law would apply to the whole layer in the limit of infinite chain length at vanishing concentrations. Of course, for finite chain lengths a characteristic length $d$ must be introduced which can be viewed as the thickness of the adsorbed polymer layer. This is often termed the distal length. A lower cutoff length $p$ also arises and is known as the proximal length. The proximal length is determined by the relative strength of the monomer-wall interaction and is typically of the order of the monomer size. For the scaling law to work, these two lengths $p$ and $d$ must be well separated.

de Gennes' argument is independent of the detailed layer structure in terms of trains, loops and tails and is therefore unable to provide any insight as to the adsorbed layer conformation apart from the overall thickness. A different approach is based on utilizing the analogy between polymer adsorption and the theory of critical phenomena. Here the minimization of an appropriate surface free energy functional is sought, with the form of the free energy chosen so as to best represent the salient features of the physics for the situation being described. Thus, different concentration levels and solvent quality necessitate different forms of the surface free energy. Recently, surface free energy functionals involving multiple order parameters (necessary for determining relative contributions of loops, tails, etc., to the polymer concentration at a given distance from the surface) have been proposed and their results compared to those of SCF [53]. In one such effort, Aubouy et al. [54] were able to improve the scaling analysis by incorporating a free energy functional approach and were thus able to describe the loop and tail size distributions. While the results obtained for the distribution close to the wall were found to be qualitatively different from that obtained via SCF, that minor drawback is outweighed by the simplicity offered.

Here it must be noted that, while insightful, these various theoretical treatments are not necessarily valid under the high solids loading regimes considered here. This is because these treatments all consider polymers interacting with an isolated surface, as in a dilute system. The effects arising from nearby interacting surfaces are thus typically neglected.
III. IN-SITU CHARACTERIZATION OF ADSORBED LAYERS

A. Fluorescence

Fluorescence and ESR spectroscopy can be used to characterize microstructure of adsorbed layers in situ. Fluorescence spectroscopy of adsorbed layers is based on changes in the photophysical response of a chromophoric molecule such as pyrene when it becomes incorporated into the layer. These photophysical changes yield valuable information on the polarity and viscosity of the microenvironment surrounding the probe [37,55-57]. For example, in the case of pyrene, aside from the

![Figure 1](image)

**Figure 1** Schematic representation of pyrene emission spectrum and its use in the determination of polymer conformation.
characteristic emission spectrum of isolated pyrene molecules – which display, among others, a peak at 374 nm – the molecule also has a tendency to form excimers (species resulting from interaction between one excited pyrene molecule and a second pyrene in the ground state) when in close proximity to each other. The fluorescence emission spectrum of such excimers exhibits a peak at around 475 nm, which is not seen in the emission spectrum of isolated pyrene molecules. By analyzing the ratio of the emission intensities at 475 nm and at 374 nm, it is therefore possible to obtain a measure of the relative intermolecular separation in pyrene-containing samples. In the case of pyrene-labeled polymer, this ratio reflects the coiled/stretched state of the polymer and is termed the coiling index, \( I_c/I_m \), where \( I_c \) is the emission intensity of the excimer peak and \( I_m \) is that of the monomer peak. In the results to be discussed here the pyrene moiety was chemically bound to the polymer chains under investigation, such that in the absence of any intermolecular interactions a high value of \( I_c/I_m \) can be taken to be indicative of a relatively coiled conformation of the polymer, while a low value would suggest a more extended conformation. This idea is presented schematically in Figure 1.

B. Electron Spin Resonance

Electron spin resonance, also known as electron paramagnetic resonance (EPR), is a form of spectroscopy that has come to be widely used for studying molecular structure and dynamics in micelles, membranes, and adsorbed films. In ESR spectroscopy, changes in the spin characteristics of a paramagnetic probe in an external magnetic field are monitored [58] in the form of absorption of microwave radiation. A unique feature of ESR spectra is that the line positions and splitting depend on the direction of the external magnetic field relative to the molecular axis. This phenomenon is called spectral anisotropy. Thus, one of the advantages of ESR over other forms of spectroscopy is its ability to resolve differently oriented paramagnetic centers. In the case of immobilized, randomly oriented (powder) spectra, therefore, anisotropic contributions from all different orientations are superimposed upon each other. Conversely, if the probe is able to rotate randomly in its environment on a timescale much faster than that of the measurement, all the anisotropy will be averaged out. This will result in a sharp three-line spectrum independent of the magnetic field direction. If, however, the molecule rotates slowly, an intermediate spectrum between that of the powder spectrum and the isotropic spectrum is obtained. This is typically the case for adsorbed polymeric probes or probes in an otherwise restricted, but not immobilized, environment. From details of the changes in the spectral line shape of this probe, it is thus possible to obtain information on the microviscosity and micropolarity of the probe environment. The former measure is obtained from the spectrum in terms of a calculated rotational correlation time, \( \tau \), while the latter is found from the measured hyperfine splitting constant [38]. Since electron pairing in chemical bonding can cause cancellation of spins, only transition metal ions and free radicals are capable of exhibit-
Figure 2: Representative ESR spectra for a nitroxide-labeled polymer and the corresponding suggested orientation/conformation. (a) Powder spectrum from nitroxide randomly and rigidly oriented. (b) Intermediate spectrum; nitroxide molecules rotate slowly, suggesting a restricted environment. (c) Isotropic spectrum for nitroxide undergoing free rotation.

The range of applications of the technique can be extended, however, by spin labeling methods whereby stable free radicals or transition metal ions are incorporated into otherwise ESR-inactive systems of interest. Thus, in this case, with the paramagnetic probe chemically incorporated into the polymer molecule, the resulting spectrum represents a measure of the orientation and behavior of the polymer molecule itself. For example, in the case of results discussed below, the rotational correlation time of ESR-sensitive nitroxide probes attached to adsorbed polymer molecules was measured. This time gives an indication of the relative ease with which the probe molecule is able to move in its environment and, there-
fore, in the case of adsorbed polymer molecules, the orientation and conformation of the molecules at the solid surface. This is illustrated in Figure 2.

Here it must be emphasized that these techniques, while applicable, are employed with difficulty in concentrated suspensions. As spectroscopic techniques, they are necessarily vulnerable to signal-to-noise limitations. These limitations are especially pronounced in concentrated systems where the noise and scatter due to the particles alone becomes excessive. The seemingly simple solution would be to use a large amount of probe-labeled polymer to increase the signal drastically. There are two important problems with this approach, however. One is that the signal from any spectroscopic experiment is an average of the signals from all the probe molecules in the sampled volume. Thus, in the cases of interest here, the observed signal represents an average of the signals from the polymer molecules adsorbed on the solid and those from polymer molecules in solution. The contributions from the two different populations of molecules, especially in such complex systems, are virtually impossible to separate from the observed spectrum. Therefore, since only the behavior of the polymer molecules actually adsorbed on the particles are of interest, it is proper to use only as much probe as is necessary to obtain a monolayer of coverage on the particles. As such, in all conformation experiments reported, the polymer concentration selected for adsorption was such that it yielded approximately 80% to 90% of a monolayer and negligible free or unadsorbed polymer. The second problem also has two parts. The first has to do with the integrity in analysis of the spectrum, primarily in the case of fluorescence. As mentioned earlier, \( L/L_\infty \) can be used as a measure of the coiling only when intermolecular interactions can be neglected. For this reason, it is often necessary to limit the amount of labeled polymer used for adsorption. The second related issue has to do with the perturbative effects of the probe moieties themselves on the system. The effect of pyrene hydrophobicity on the solution behavior of pyrene-containing systems has been established [59,60]. More recently, direct evidence of the significant flocculation effects caused by the pyrene label in a suspension containing adsorbed pyrene-labeled polymer has been obtained [61].

The use of these techniques therefore requires a balance between having as much labeled polymer as necessary to provide sufficient signal and as little polymer so as not to have any significant free polymer in solution or any intermolecular probe-probe interactions. In all the work to be reported here, the total amount of polymer used is such that there is negligible free polymer after adsorption, and the labeled polymer is mixed with unlabeled polymer in amounts of 3% or less to negate any adverse intermolecular interactions. Indeed, the argument can still be made that the behavior of the labeled polymers does not necessarily reflect that of the unlabeled polymers at the surface. This statement can be made for essentially all techniques in which it is necessary to significantly modify the species of interest in order to observe it. While it is not possible to unequivocally refute that possibility in this case, it is felt that the precautions taken and the evidence pro-
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vided by auxiliary experiments provide reason to believe that the conformational behavior observed for the labeled molecules is similar to, if not conclusively representative of, that of the unlabeled polymer molecules as a whole.

IV. EXPERIMENTAL OBSERVATIONS

As stated earlier, there are virtually no reports on measurements of polymer conformation in concentrated suspension systems. As such, the findings reported here are drawn primarily from the results of our own work in the area.

A. Materials

The results discussed here were obtained from tests with two systems: polyethylene oxide (PEO)–silica and polyacrylic acid (PAA)–alumina. Both these systems are of significant industrial importance. The individual constituents have also been widely studied separately.

The alumina used was AKP-50 powder obtained from Sumitomo Chemical. The average particle diameter was 0.2 μm and the specific surface area as determined by nitrogen B.E.T. adsorption was 10.9 m² g⁻¹. The silica was obtained from Geltech Inc. and had a nominal particle size of 1 μm and a specific surface area of 4.2 m² g⁻¹.

Unlabeled PAA with a molecular weight of 90,000 was purchased from Polysciences Inc. Pyrene-labeled PAA with a pyrene content of roughly 0.75%, and a molecular weight of 76,000 was custom-synthesized by National Chemical Lab, India. Nitroxyl-labeled PAA with a molecular weight of 95,000 and a labeling ratio of 1:100 (molar basis) was prepared by Nalco Chemical Company.

Unlabeled PEO with average molecular weight between 6,000 and 7,500 was obtained from Polysciences Inc. Pyrene-labeled PEO, with a 1% pyrene content and a molecular weight of 7,500, was synthesized by the University of Florida.

A 0.03 M sodium nitrate solution was used, for ionic strength control, in preparing all suspensions.

B. Methods

1. Polymer Adsorption

Polymer adsorption was monitored by determining depletion of the polymer from the solution after equilibration with the solids under controlled pH conditions using total organic carbon analysis.
2. Polymer Conformation

The conformation of pyrene-labeled PEO and PAA was determined by analyzing the fluorescence spectra from the suspensions collected using an LS-1 fluorescence spectrophotometer (Photon Technology International Inc.).

The orientation of the nitroxyl-labeled PAA was monitored by determining the first derivative of the ESR absorbance spectrum from the sample suspensions. Spectra were collected using a Model 8300 ESR/EPR X-Band Spectrometer (Micro-Now Instrument Company).

V. RESULTS

A. Adsorption

The adsorption density of PAA on alumina at both pH 4 and pH 9 is shown in Figure 3 as a function of solids loading (solids volume percent). Interestingly, it is clear that solids loading has a marked effect on the adsorption density of polyacrylic acid at the alumina-solution interface. As the alumina suspension becomes more concentrated, the adsorption density decreases, irrespective of the pH. This

![Figure 3](image-url)

Figure 3  Adsorption density of polyacrylic acid on alumina as a function of solids loading at pH 4 and 9.
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behavior is especially evident at relatively low solids loading levels (below 10 – 15 volume percent). Also evident is the pH effect on PAA adsorption density, with the adsorption density at pH 4 being higher than that at pH 9 throughout the entire solids loading range. This is readily attributed to electrostatic contributions insofar as a more positively charged alumina surface at pH 4 is more likely to attract the negatively charged polymer.

Figure 4 gives the adsorption density of polyethylene oxide on silica at pH 4 as a function of solids loading. Here again, increase in solids loading is found to result in a decrease in the adsorption density of the polymer, this effect also being more pronounced at low solids loading. This result is interesting since any explanation for the observed adsorption behavior based on electrostatics is ruled out, PEO being a nonionic polymer. It may therefore be necessary to consider explanations perhaps based on conformational changes of the adsorbed polymer layer as the interparticle distance decreases with increase in solids loading.

It is to be noted here that these adsorption experiments were all carried out at the same fixed initial concentration of the polymer. Since increase in solids loading does necessarily result in greater depletion of the polymer from solution, each experiment at a higher solids loading is actually operating at a lower residual polymer concentration. This decrease in equilibrium residual concentration could be a reason for the decrease in adsorption density as illustrated in Figure 5. The initial concentrations used in the experiments reported here were, however, chosen
to be roughly an order of magnitude higher than those required to yield a monolayer of polymer coverage. Hence, the above explanation might not be applicable in the present case.

In an effort to further examine this phenomenon, adsorption of PAA on alumina was repeated using a reduced initial polymer concentration only roughly 30% greater than that required for the so-called plateau adsorption. These results are presented in Figure 6, alongside the earlier results. While the pH effect on the adsorption density is still evident, the effect of solids loading is no longer seen. The reason for this behavior is as yet unclear. One possible explanation may have to do with precipitation or multilayer adsorption of the polymer onto alumina at low solids loading in the earlier work. Addition of a few alumina particles to a solution at high polymer concentrations may in fact "seed" the precipitation or multilayer adsorption of PAA on alumina. Thus the apparent 'adsorption density' is greatly increased. As more solids are added, however, surface area for adsorption is no longer limited and the adsorption density approaches the "real" value. Thus the coincidence of both sets of experimental data at high solids loading may be explained. It must be acknowledged that this is but one of several possible explanations for the discrepancy observed and further study is required to solve the
Figure 6  Adsorption density of polyacrylic acid on alumina at reduced initial concentrations (~1.3 C_{max}, where C_{max} is the initial polymer concentration required for plateau adsorption), alongside those obtained at a fixed elevated initial concentration (dashed lines).

problem unambiguously. Still, these findings underscore the necessity for careful experimental design and analysis when conducting even the most routine measurements with concentrated suspensions.

B. Conformation and Orientation

The conformation and orientation of the adsorbed polymer molecules were obtained in situ using the fluorescence and ESR spectroscopy techniques described earlier.

The coiling index of polyacrylic acid adsorbed on alumina is shown in Figure 7. As mentioned above, since the adsorption density does change with solids loading, that variable was eliminated by carrying out the fluorescence measurements at a constant adsorption density, also given in the figure. The coiling index of the adsorbed PAA is seen to decrease significantly with increasing solids loading despite having the adsorption density kept constant. This result shows that the
Figure 7  Coiling index of adsorbed polyacrylic acid on alumina as a function of solids loading.

Figure 8  Coiling index of polyethylene oxide adsorbed on silica as a function of solids loading.
adsorbed polyacrylic acid molecules tend to become extended as the solids loading is increased.

The coiling index of the polyethylene oxide adsorbed on silica displays a similar behavior as revealed in Figure 8. This set of experiments is also carried out at a constant adsorption density as indicated on the figure.

In this case also, the coiling index of polyethylene oxide is found to decrease with increase in solids loading. Thus, again evidence is obtained for polymer adsorption behavior as a function of solids loading being relatively independent of electrostatic considerations.

ESR spectroscopy also was employed in the case of the polyacrylic acid-alumina system to obtain complementary information on the orientation of the polymer at the solid-liquid interface. Representative spectra for three different solids loading values are shown in Figure 9 along with the spectrum for the solution for comparison purposes.

The so-called “free rotational component” of the spectra at about 3240 Gauss is indicated on the figure. Surprisingly, this component (a measure of the
unrestricted portion of the adsorbed polymer) is found to increase with solids loading, suggesting that the adsorbed PAA becomes less restricted in its motion as solids loading is increased. A more quantitative measure of the adsorbed polymer mobility is the rotational correlation time, $\tau$, mentioned earlier. This value was calculated for the three solids loadings studied and the results are given in Figure 10. This figure corroborates the inferences from Figure 9 in that the polyacrylic acid becomes less restricted with increase in solids loading.

These results suggest that the adsorbed PAA molecule tends to dangle more into solution and/or adopts a conformation with more 'loops' and 'tails' as solids loading is increased. This idea, while at first counter-intuitive, is, in fact, sound. Consider the alumina surface to have a polyacrylic acid coverage close to that of a monolayer (as in the cases discussed here). It is known from the fluorescence spectroscopy results that the adsorbed PAA extends as the solids loading is increased. However, since the surface coverage was already at or near a maximum, there is little bare space for the polymer to be able to stretch out along the particle surface. For the polymer to extend, it then has no choice but to do so in a direction away from the particle surface. This will indeed result in a more 'dangling' con-

![Figure 10](image-url)

**Figure 10** Rotational correlational time for polyacrylic acid adsorbed on alumina as function of solids loading.
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formation and/or those with more 'loops' and 'tails'. This idea is expressed schematically in Figure 11.

While these results may at first seem to fly in the face of conventional wisdom (which holds that the average conformation of a polymer should be described by a single parameter, \( v \), the Flory exponent) it is important to recognize that this need not be so. While the Flory exponent for a given solvent is commonly known to depend upon typical bulk solution parameters such as temperature and pH, the possibility of other factors influencing \( v \) have not been considered. In the present case, for example, though bulk solution conditions may not change measurably, the possibility of local variations in the vicinity of the particle surface has to be

![Figure 11 Schematic two-dimensional representation of conformational changes as a function of increasing solids loading.](image-url)
allowed for. In particular, as solids loading increases and interparticle separation falls, polymers on any one surface will begin to "feel" the effects of its nearest neighbors. Conformational responses to such external force fields have not been well-studied in the context of traditional Flory exponent arguments. Still, it is realized that the effects seen here begin to be observed even at relatively large interparticle separations, so there may remain other factors to be considered. One such possibility may be local aggregation.

The implications of these changes in conformation in the behavior of the suspension must naturally be considered as they can affect the measurable properties of the suspension. While it is relatively difficult to make measurements with highly concentrated suspensions, it is possible to conduct experiments at relatively low solids loading to get some understanding of potential effects. Such an experiment was undertaken wherein the settling rate of an alumina suspension with adsorbed PAA was monitored as a function of pH. The coiling index of the adsorbed PAA was also measured for the same suspensions. The results of this experiment are given in Figure 12. It can readily be seen that extension of the adsorbed polymer results in a marked increase in the settling rate of the suspension. This is at-

Figure 12 Coiling index and settling rate of a polyacrylic acid-alumina suspension; effect of adsorbed polymer conformation on suspension behavior.
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tributed to increased bridging between particles in the suspension as the polymer molecules become more extended.

Even though the results presented here indicate significant advances in our ability to monitor the behavior of adsorbed polymers in highly concentrated solid suspensions, much remains to be done to gain a fuller understanding of this behavior. Local probes of solvent quality at the microscale are needed so that theories of adsorbed polymer conformation can be extended to high solids loading systems. In addition, we have neglected any mention here of the dynamics involved in the behavior of adsorbed polymers and how it may impact properties of the suspension. Thus there remain many fruitful areas of research in this complex but important field.

VI. SUMMARY

Concentrated suspensions are of much industrial importance and academic interest. Due to their complexity, the behavior of these suspensions is often difficult, if not impossible, to predict. As a result, empirical solutions involving polymer and surfactant additives are often employed as a means of controlling the properties of these dispersions. The analysis of the effects of these additives on suspension performance has been lacking due to an inability to monitor their properties, such as conformation and orientation, in situ. Results discussed here show the feasibility of monitoring both conformation and orientation of adsorbed polymer layers in situ in concentrated suspensions using fluorescence and electron spin resonance techniques. The techniques and precautions have been described, along with an example of significant correlation of the conformation of adsorbed polymer to flocculation/dispersion behavior of the suspensions.

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