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Laponite Dispersions in the Presence of an Associative Polymer

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Sedimentation and viscometric properties of a dilute Laponite dispersion are studied in the presence of an associative polymer, hydrophobically modified (hydroxypropyl)guar, and its nonassociative precursor, focusing on the specific influence of intermolecular associations. The hydrophobic groups do not take a significant part in the adsorption process. The main difference between the associative and the nonassociative polymers appears at polymer concentrations above complete coverage of the clay mineral. In this concentration range and up to the overlap concentration, nonassociating macromolecules lead to the formation of freely suspended entities, whose size did not depend on the polymer concentration. The associating macromolecules, in the same concentration range, lead to aggregation of the particles, the degree of which depends on the polymer concentration. This behavior is attributed to the formation of associating junctions between adsorbed and/or nonadsorbed polymers.

Introduction

Natural swelling clay minerals, especially montmorillonites, are used in various industrial products and processes as rheology modifiers and stability controllers; for instance, they are used most extensively in drilling fluids and muds. In many research works on the macroscopic properties of swelling clays, Laponite, a platelike synthetic hectorite-type clay, is used as a model system, mainly because of its high purity. When dispersed in aqueous media, Laponite particles are shown to lead to the formation of either gel-like structures or free flowing suspensions or phase-separated flocs.[1−7] As far as the dilute regime is concerned, two microstructural pictures have been proposed: the primary entities in the dispersions are either the individualized discrete disklike Laponite particles[2] or tactoids, composed of two to four parallel Laponite platelets separated by a few water layers.[8]

In many industrial applications or in nature, swelling clay minerals are used in the presence of polymers, which control both stability and flocculation behavior. The literature is mainly concerned with adsorption properties, their connection with flocculation mechanisms and aggregate formation.[9−12] Among numerous polymer/clay systems, attention was paid to polysaccharide/clay systems, mainly in the field of soil science where polysaccharides are known to stabilize soil aggregates.[13]

Whereas the adsorption of synthetic and natural polymers on clay particles was the subject of many investigations, literature is scarce concerning adsorption mechanisms and related properties of associative polymers on clay minerals.[14] Associative polymers constitute a class of macromolecules bearing few attractive groups which can associate to form weak reversible physical bonds.[15] Such polymeric systems are extensively used in the formulation of many industrial products as rheology modifiers or flocculents.[16]

The aim of the paper is to study the influence of intermolecular associations on the hydrodynamic properties of Laponite dispersions in a dilute regime.

Experimental Section

Laponite. The clay particles used in this work are Laponite particles, commercialized by Baroid Ltd. (Aberdeen, Scotland) and referenced as Therma Vis. When fully delaminated, they are platelets, which can be compared to disks with a diameter of 30 nm (disk area of about 700 nm²) and a thickness of 1 nm;[2] their density is 2.5 g/cm³, and their specific total surface area is about 360 m²/g.[17] This synthetic clay is mainly composed of SiO_2 (about 66%) and MgO (about 30%).

Polymers. The polymers used in this study were supplied by Lamberti s.p.a. (Albizzate, Italy). They are of two types: the precursor, a nonmodified (hydroxypropyl)guar (HPG), and the hydrophobically modified sample (HMHPG), obtained by reaction of the precursor with a mixture of C_{18} to C_{28} *n*-alkyl epoxides. Figure 1 shows the structure of the repeating unit of (hydroxypropyl)guar.

Both polymers have nearly the same molecular characteristics: the weight-average molecular weight is $\sim2 \times 10^6$, corresponding to a degree of polymerization of ∼3000, and the polydispersity index is ∼1.5. The intrinsic viscosity of HPG macromolecules is ∼1200 cm³/g, and that of HMHPG is ∼960 cm³/g. The radius of gyration of the slightly stiffened random-coil HPG macromol-

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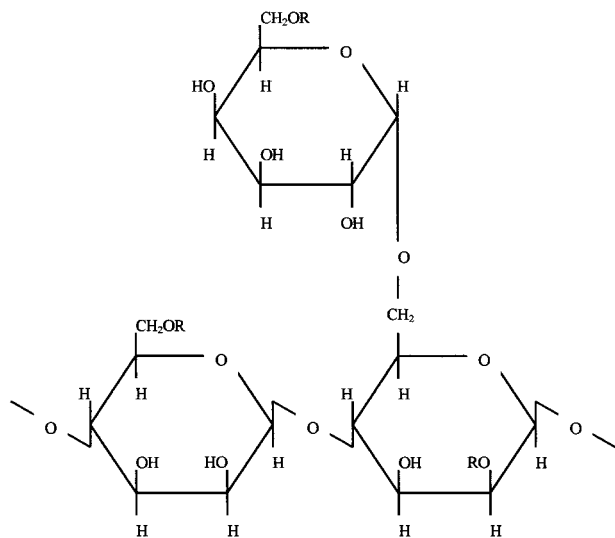(17) Fripiat, J.; Cases, J.; François, M.; Letellier *J. Colloid Interface Sci.* **1982**, *89*, 378.

Figure 1. Repeating unit of (hydroxypropyl)guar (R = CH$_2$-CH$_2$CH$_2$OH).

ecules is ~90 nm, and the value is ~80 nm for HMHPG, which is in a slightly more compact conformation due to the effect of intramolecular associations.[18] The hydrophobic substituents are randomly distributed along the macromolecular backbone, and the average number of alkyl groups per chain is expected to lie between 0 and a few tens.[19] The rheological properties of these polymers were thoroughly studied at different concentrations and under different experimental conditions.[20-23]

HPG and HMHPG/Laponite Dispersions. All samples tested in this work were prepared by following the same protocol: in a first step, a 6000 ppm polymer solution and a 4×10^{-2}% Laponite suspension were prepared at room temperature and at a fixed ionic strength of 10^{-3} M in NaCl. In a second step, the polymer solution was diluted in order to obtain the final desired polymer concentration, which lies between 50 and 2500 ppm, and then Laponite particles were added so that the solid volume fraction equals 8×10^{-3}%, that is 2×10^{-2}% in weight. The samples were then moderately stirred during 2 h and left at rest for 1 day before any measurement. pH was measured for all samples tested and was about 9; working at such pH values avoided the dissolution of the Laponite particles.[24]

Adsorption Measurements. Before any adsorption measurement, the samples were centrifuged at 18 000 rpm at 25 °C during 1 h in order to separate Laponite particles covered by polymer macromolecules, located at the bottom, from the nonadsorbed macromolecules located in the supernatant. Then, two experimental techniques were used to measure the equilibrium concentration of the free polymer chains, C_{equ}.

The first method was based on a viscometric measurement: Newtonian viscosity of the polymer solution was first determined as a function of concentration; the equilibrium concentration was then obtained from the viscosity level of the supernatant.

The second method was based on direct concentration measurement by the total organic carbon (TOC) technique: a small sample of supernatant was heated at 680 °C in an O$_2$ atmosphere, so that all carbon atoms were transformed in CO$_2$, whose concentration was determined by spectrometry; through knowledge of the chemical structure of HPG and HMHPG, the free polymer concentration was determined.

For both techniques, the polymer adsorbed amount was calculated from the difference between the initial polymer concentration and the equilibrium concentration.
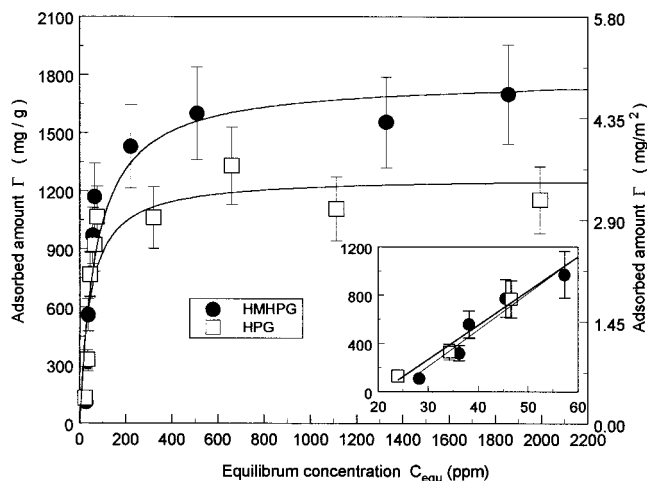
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Figure 2. Adsorption of HPG and HMHPG on Laponite particles at a volume fraction of 8×10^{-3}%.

Both techniques were shown to lead to comparable qualitative and quantitative results at the plateau of the adsorption isotherm. The TOC technique was more accurate and allowed the determination of the adsorption isotherm at very low equilibrium concentrations. All experimental results presented in the paper were obtained from the TOC technique.

The experimental error in the determination of the amount of adsorbed polymer is estimated to lie within 15%.

Viscometry. All viscometric measurements have been performed at 25 °C with a Low-Shear 30 viscometer, equipped with a Couette geometry with a gap of 0.5 mm. Great care was taken to avoid sedimentation during the measurement of the viscosity of HPG and HMHPG/Laponite dispersions. Sedimentation of all samples tested was shown to be insignificant during about 30 min, so the duration of all viscometric tests was limited to 20 min.

Sedimentation. The sedimentation tests were performed to determine the sediment volumes of HPG and HMHPG/Laponite dispersions after gravity settling. The containers were glass cylinder test tubes with an inner diameter of 26 mm and a height of 225 mm.

Results

Adsorption. Figure 2 shows the adsorption isotherm of HPG and HMHPG on Laponite particles, for initial polymer concentrations up to 2500 ppm. Both polymers have the same qualitative adsorption properties: a sharp increase of the adsorbed amount with an increase of equilibrium concentrations, for equilibrium concentrations below about 200 ppm; and the existence of a plateau for equilibrium concentrations between 200 and 2000 ppm.

These adsorption isotherms can be correctly fitted to the well-known Langmuir equation:

$$\frac{\Gamma}{\Gamma_m} = \frac{KC_{equ}}{1 + KC_{equ}} \qquad (1)$$

where Γ_m is the saturated adsorption and K is the equilibrium constant, in the very dilute limit. This model has been originally proposed to describe the adsorption of nonpolymeric monofunctional solutes. Still, it has been applied rather successfully to the description of the adsorption isotherm of many polymer/particle systems, including associative polymer/particle systems,[25] even though it is difficult to give a clear physical significance

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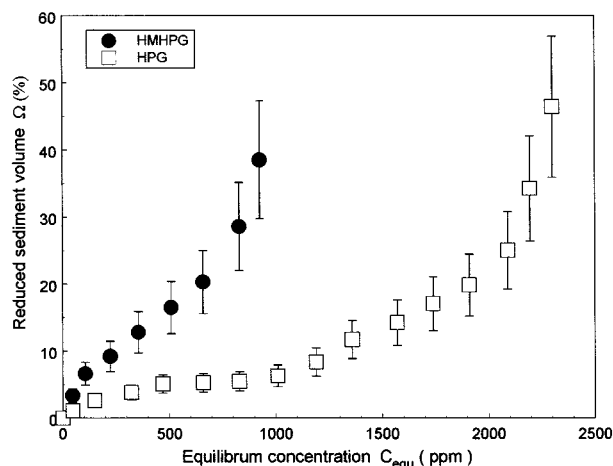(25) Pham, Q. T.; Russel, W. B.; Lau, W. *J. Rheol.* **1998**, *42*, 159.

Figure 3. Reduced sediment volume of HPG/Laponite and HMHPG/Laponite dispersions at a volume fraction of 8×10^{-3}% as a function of the free polymer concentration.

to the Langmuir parameters Γ_m and K.[26] Equation 1 is used as a fit equation to determine the quantitative characteristics of the adsorption isotherm. These empirical parameters are (i) the isotherm plateau value Γ_m and (ii) the equilibrium constant K which characterizes the interaction between the adsorbing macromolecule and the Laponite surface and somewhat quantifies the affinity of the macromolecules to the solid surface.[13]

These two fitting parameters show that there are slight quantitative differences between the two polymers adsorbing onto the Laponite particles: $\Gamma_m = 1300$ mg/g for HPG, that is, ~3.5 mg/m², or 850 nm²/chain, and $\Gamma_m = 1800$ mg/g for HMHPG, that is, ~5 mg/m², or 600 nm²/chain. $K = 22\,000$ g/g for HPG, and $K = 18\,000$ g/g for HMHPG.

Sedimentation. Sedimentation occurs at initial polymer concentrations below 3000 ppm ($C_{equ} = 2300$ ppm) for HPG/Laponite and below 1500 ppm ($C_{equ} = 1000$ ppm) for HMHPG/Laponite. Above these concentrations, the samples are stable for very long times. During sedimentation, a distinct interface between the dispersion and the supernatant is not observed. This result makes impossible any determination of settling rates.

The reduced sediment volume Ω (ratio of the sediment volume to the initial sample volume) for HMHPG/Laponite is larger than for HPG/Laponite at any equilibrium polymer concentration (Figure 3). The dependence of Ω on C_{equ} is significantly different for the two systems.

Viscometry. The comparative viscometric study is limited to equilibrium polymer concentrations below 700 ppm; for higher concentrations, the dispersing medium of the HMHPG/Laponite samples is difficult to investigate, as discussed further in the paper. The flow curves clearly show that the viscosity of all suspensions and dispersing media tested exhibit a Newtonian plateau at low shear rates, even if its value is not directly measurable (Figures 4–7). The zero-shear Newtonian viscosity, η_0, of all samples was determined by fitting the flow curves to the Cross model:[27]

$$\frac{\eta(\dot{\gamma}) - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\dot{\gamma})^n} \tag{2}$$

where $\eta(\dot{\gamma})$ is the apparent shear viscosity, η_∞ refers to the

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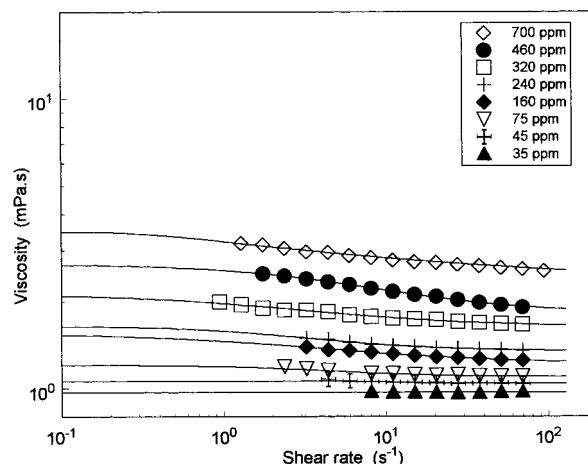(27) Cross, M. M. *J. Colloid Sci.* **1965**, *20*, 417.

Figure 4. Viscosity of HPG/Laponite dispersions at a volume fraction of 8×10^{-3}%; solid lines: Cross model.
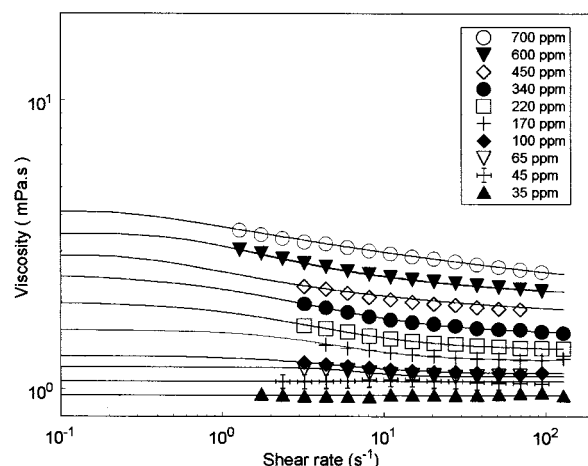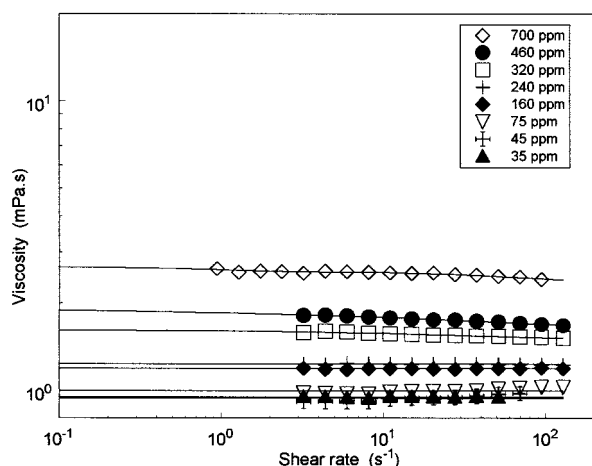

Figure 5. Viscosity of HMHPG/Laponite dispersions at a volume fraction of 8×10^{-3}%; solid lines: Cross model.

asymptotic value at very high shear rates, and K and n are constant parameters.

To quantify the relative hydrodynamic contribution of the dispersed particles, we considered the specific viscosity, η_{sp}, defined as the difference between the suspension Newtonian viscosity, η, and that of the continuous dispersing phase, η_s, divided by η_s:

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \tag{3}$$

In Figure 8, we plotted η_{sp} as a function of the equilibrium concentration C_{equ}. The relative hydrodynamic contribution of the solid content is similar for both polymers up to $C_{equ} = 200$ ppm, that is, precisely for polymer concentrations below the concentration needed to saturate the surface of the Laponite particles. Beyond this concentration, the relative contribution of the solid particles to the viscosity depends on the nature of the polymer: it is constant in the case of HPG; it increases linearly with the HMHPG concentration up to $C_{equ} = 500$ ppm and then decreases.

Discussion

The adsorption results indicate that both polymers have nearly the same affinity to the clay mineral surface; indeed, the equilibrium constant K for HMHPG/Laponite is only 18% lower than that for HPG/Laponite. This result reveals

Figure 6. Viscosity of HPG supernatants obtained after gravity settling of HPG/Laponite dispersions at a volume fraction of 8×10^{-3}%; solid lines: Cross model.
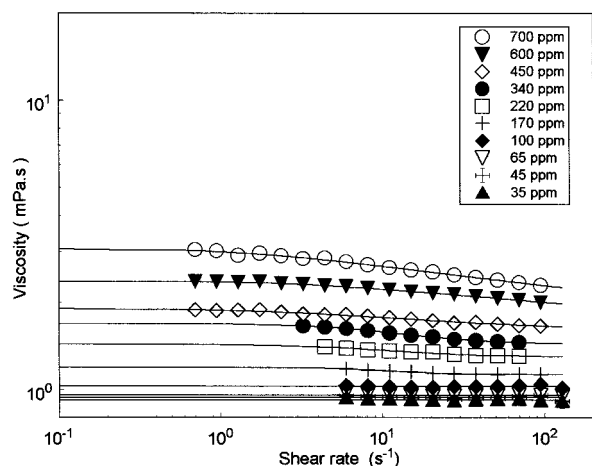

Figure 7. Viscosity of HMHPG supernatants obtained after gravity settling of HMHPG/Laponite dispersions at a volume fraction of 8×10^{-3}%; solid lines: Cross model.
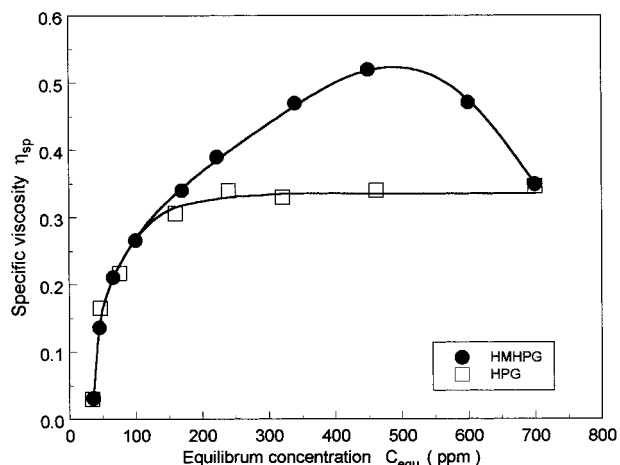

Figure 8. The specific viscosity of HPG/Laponite and HMHPG/Laponite dispersions at a volume fraction of 8×10^{-3}% as a function of the free polymer concentration.

that hydrophobic groups are either not directly involved in the adsorption mechanism or not numerous enough to have a significant contribution to adsorption. Interactions between HPG or HMHPG and the Laponite surfaces are expected to be mostly mediated by hydrogen bonds between the hydroxyl groups on the macro-

molecular chains and the oxygen atoms at the Laponite surface.[28]

There are also differences. The amount of polymer adsorbed on the Laponite particles at surface saturation is about 30% lower for HPG, compared to HMHPG. This result cannot be explained by differences in the molecular weight or the affinity of the two polymers to the clay mineral surface but could be attributed to the slightly more compact conformation of the HMHPG chains. Another explanation could be the possible formation of multiple layers through hydrophobic associations, as suggested by some authors to explain the specific adsorption of some hydrophobically modified polymers on solid surfaces.[25,29] This latter explanation seems to us to be less likely, because the shape of the adsorption isotherm shows a plateau and not a continuous increase as observed in the cited works.

The sedimentation and zero-shear viscometric measurements indicate three regions:

At low polymer equilibrium concentrations ($C_{equ} < 200$ ppm), corresponding to a partial coverage of the clay mineral surfaces, both systems behave in a similar way, at least qualitatively. Adsorption of HPG or HMHPG on Laponite increases the volume of the dispersed particles or tactoids, by increasing the adsorbed layer thickness as the polymer adsorbed amount approaches full coverage. The only difference is that the volume of these entities is somewhat higher for HMHPG, as revealed by the sedimentation data. This result is expected insofar as more HMHPG is adsorbed than HPG at any polymer concentration.

At 200 ppm $< C_{equ} < 1000$ ppm, the sediment volume and the flow resistance of suspended particles are constant for HPG/Laponite and increase with C_{equ} for HMHPG/Laponite. For HPG/Laponite, the sedimentation and zero-shear viscosity clearly show that dispersed objects have the same hydrodynamic volume over the whole range of relevant polymer concentrations. Thus, at full Laponite surface coverage, adding HPG molecules only contributes to increase the viscosity of the dispersing medium. On the other hand, for HMHPG/Laponite the increase of the sediment volume with increasing C_{equ} indicates that the effective hydrodynamic volume increases with the amount of HMHPG, at least in the concentration range 200 ppm $< C_{equ} < 500$ ppm. The suspended objects retain more and more nonadsorbed macromolecules via intermolecular hydrophobic association. The opposite effect is observed for the zero-shear viscosity at free polymer concentrations of 500 ppm $< C_{equ} < 1000$ ppm and is attributed to the increasing influence of the hydrophobic interactions between the chains of the free macromolecules, which increases the viscous contribution of the suspending medium. In this concentration regime, the hydrophobic interactions between free polymers prevail over the hydrophobic interactions between adsorbed and nonadsorbed macromolecules.

At $C_{equ} > 1000$ ppm, no gravity settling is observed for HMHPG/Laponite, and the sediment volume and relative contribution to viscosity of dispersed particles increase with C_{equ} for HPG/Laponite, followed by a no-settling regime. It is the domain where macromolecular entanglements between the chains of free polymer are present and prevail. The overlap concentration, which can be estimated as the inverse of the intrinsic viscosity, is about 1000 ppm

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for both polymers. Thus, above this concentration threshold, the increase of the sediment volume and relative contribution to viscosity of dispersed particles is attributed to the topological interactions between the chains of free polymers, which hinder the Laponite particles from settling under gravity. This effect is reinforced in the case of HMHPG, because of the presence of numerous intermolecular hydrophobic interactions which "strengthen" entanglements in this concentration range,[20] and the no-settling region appears at lower equilibrium concentrations. In this concentration domain, the samples can be considered as moderately dense polymer solutions enriched with few Laponite particles.

Conclusion

The adsorption study has shown that the associative polymer and its precursor have nearly the same affinity to the Laponite surface, the adsorbed amount at surface saturation being nevertheless somewhat larger for the hydrophobically modified chains.

The sedimentation and viscometric measurements indicate three domains:

Below the concentration corresponding to saturation of the surface, both adsorbed polymers increase the hydrodynamic volume of the suspended objects.

From polymer concentrations corresponding to surface saturation up to the overlap concentration, the nonmodified polymer only increases the viscosity of the dispersing medium, whereas the modified macromolecules induce hydrophobic interactions between the chains of adsorbed and nonadsorbed polymers and, as concentration increases, between the chains of free polymer.

From the overlap concentration, where entanglements and intermolecular associations prevail, the modified polymer/Laponite systems are macroscopically stable; this transition appears at higher free polymer concentrations for the nonmodified polymer/Laponite systems, for which associations are absent.