

Polyoxyethylene Di-Phosphonates as Efficient Dispersing Polymers for Aqueous Suspensions

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ABSTRACT: Polyoxyethylenes having a di-phosphonate functional group at one of their chain ends strongly adsorb on calcium carbonate particles in aqueous colloidal suspensions. An enhanced colloidal stability of such suspensions results with a concomitant drastic reduction of the viscosity of concentrated aqueous suspensions. The viscosity of a 20 wt % CaCO₃ colloidal suspension in water could be lowered to 2 mPa · s with low concentrations of polymer. The adsorption and viscosity reduction were studied as a function of the chemical nature of the end chain group and the polymer molecular weight. The di-phosphonate group was found the most efficient anionic group when associated with a polyoxyethylene of polymerization degree larger than 20. The main features of this di-block architecture of the polymer are discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2545–2555, 1997

INTRODUCTION

The dispersion of inorganic particles as a colloidal suspension in a solvent or a polymer matrix requires the use of some dispersing agent that adsorbs at the surface of the particles.¹ Most efficient dispersing agents are polymers that have to be selected according to the chemical nature of the particle surface and the type of dispersing medium.² Colloidal dispersions can be found in a wide range of applications such as mechanical reinforcement of polymeric materials with inorganic fillers, pigment dispersion in organic coatings and thickening of suspensions, and emulsions. Among the wide variety of specific problems, the dispersion of calcium containing inorganic particles in water is encountered in several important applied domains, mainly for the use of calcium carbonate

as a pigment in painting and paper coating compositions,³ and for the control of cement paste rheology and concrete mechanical strength.^{4,5} Anionic polymers such as polyacrylates^{6,7} or sulfonated resins (poly-naphthalene sulfonates)^{4,8} are most commonly used where the colloidal stability arises from both repulsive electrostatic forces and the steric barrier due to polymer adsorption.²

Polymer adsorption on a surface involves chemical groups that have some affinity for the surface groups of the solid particle. For a homopolymer or a random copolymer, these groups that are responsible for the adsorption are distributed at random along the macromolecular chain and the structure of the polymer adsorbed layer then consists of adsorbed segments that lay flat on the surface, and nonadsorbed loops and tails that ensure the steric stabilization of the particles.^{2,9–17} If steric stabilization of particles is aimed for, strong adsorption of a thick polymer layer is required. If the functional groups of the polymer have a strong affinity for the particle surface groups, the macro-

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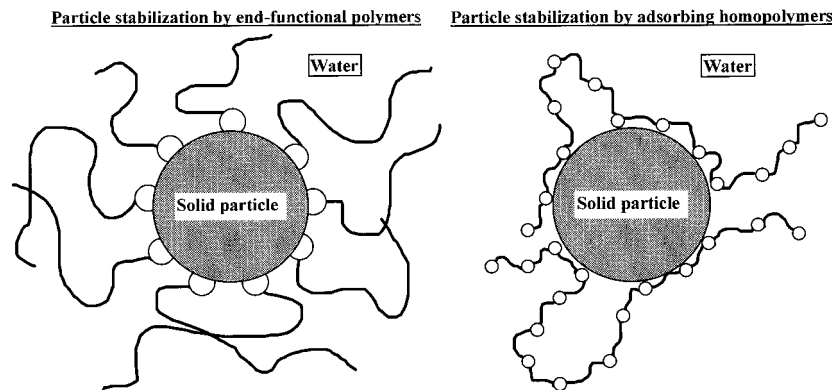


Figure 1 Adsorbed polymer steric stabilization of colloidal particles.

molecules adsorb as a flat collapsed layer, which is too thin for efficient steric stabilization. A thick and strongly adsorbed layer can be obtained in the case of low adsorption energy per functional group with high molecular weight polymers, because the weak adsorption energies of each functional group of the polymer add up, giving a large total adsorption energy per macromolecular chain. However, particle destabilization may occur by a polymer bridging mechanism for long chains, leading to flocculation.¹⁷ The molecular weight has then to remain moderate, and a compromise has to be found by the control of both the adsorption energy per functional group and the polymer molecular weight.

In the present work, nonadsorbing polymers having a functional group at one of their chain ends that ensures adsorption are studied. The structure of the adsorbed polymer layer is then completely different, consisting essentially of free tails (Fig. 1). This di-block molecular architecture allows a decoupling of the surface adsorption and steric stabilization functions so that both properties can be modified at will independently of the other one. The choice of the functional group determines the adsorption energy. An efficient steric stabilization by the polymer part of the macromolecule requires that the polymer forms a thick layer at the particle surface from which other polymer-coated particles are expelled. The polymer is then chosen such that it does not adsorb on the surface (except by its functional end) and such that the dispersing medium is a "good solvent." The polymer molecular weight and solvent quality determine the adsorbed layer thickness.

The influences of both functional group and polymer molecular weight are studied in the case of stabilization of calcium carbonate particles in

water. Polyethylene oxide (PEO) is chosen as the polymer part because water is a good solvent of PEO at room temperature and the studied functional groups are carboxylate, sulfonate, phosphonate, and di-phosphonate, which all have some affinity for calcium containing inorganic surfaces. The structure of such polymers is reminiscent of that of surfactants, and some similarities are expected. In particular, it is noticed that classical nonionic surfactants that are widely used in the stabilization of emulsions have a small hydrophobic alkyl chain that ensures adsorption and quite a long polyethylene oxide part (with 10 to 20 ethylene oxide units) for steric stabilization.

The structure of the layer of polymers adsorbed (or chemically grafted) by their chain end depends on the molecular weight and solvent quality as well as the grafting density. Two regimes have been observed experimentally,^{18–22} in agreement with theory^{9–11,23–29} (Fig. 2). A "mushroom" regime at low coverage where adsorbed macromolecules are independent of each other and have a coil conformation similar to that found in a dilute solution; the thickness of the polymer layer is equal to the polymer radius of gyration. When the grafting density is increased, polymer coils overlap and a "brush" regime is reached where the structure of the adsorbed polymer layer is similar to that of a semidilute solution. The crossover surface coverage between these two regimes is analogous to the dilute-to-semidilute concentration C^* in bulk polymer solutions.

EXPERIMENTAL

Materials

The following nonionic water soluble polymers containing anionic groups at their chain end have been studied:

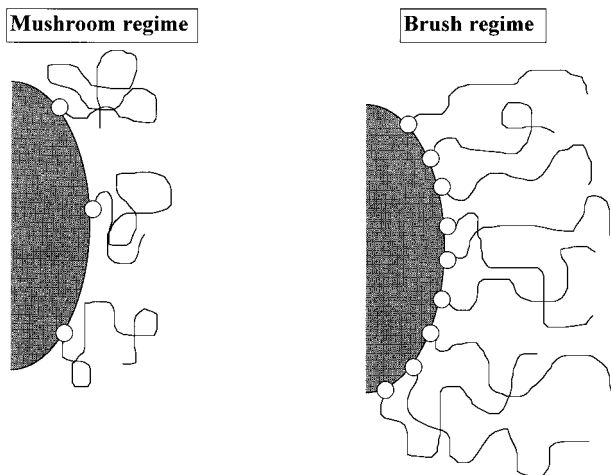
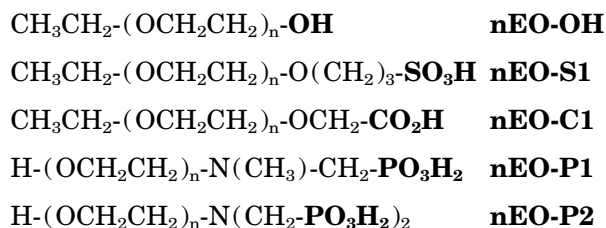


Figure 2 Structure of chain end adsorbed polymers for low and high surface coverage.



The PEO–monoethyl ether (nEO-OH) was synthesized by conventional anionic polymerization of ethylene oxide initiated by potassium ethoxide in dry THF medium.^{30,31} The sulfonate (nEO-S1) terminated polymers have been prepared by end capping with 1,3-propane sultone the nEO-OH polymer at the end of the anionic polymerization.^{30,32} The carboxylate (nEO-C1) terminated polymers have been prepared from the corresponding nEO-OH polymers by oxidation of the alcohol group to a carboxylic acid by pyridinium dichromate^{30,33} or by reacting ethyl bromoacetate with the sodium alcoholate of nEO-OH^{30,34,35} followed by hydrolysis of the ester group by aqueous sodium hydroxide. The nEO-P1 and nEO-P2 polymers where P1 and P2 are mono- and di-phosphonate functionality have been prepared starting from primary and secondary amino-polyoxyethylenes obtained by anionic polymerization of ethylene oxide initiated by potassium aminoalcoholates.^{30,31} The mono- and di-phosphonates were prepared by means of the Mannich–Moadritzer reaction.^{30,36} The polymers molecular weight distributions as measured by size exclusion chromatography and FAB⁺ mass spectroscopy are narrow^{30,31}; the polydispersity indices ($I_p = M_w/M_n$) are lower than 1.2 for all polymers.

The calcium carbonate is an additive-free precipitated calcite powder purchased under the trademark Socal 31 from the Solvay Company. Electron microscopy shows that the 70 nm diameter CaCO_3 particles are aggregated into large porous flocs of low density. The specific surface area measured by the nitrogen BET method is $22 \text{ m}^2/\text{g}$. The isoelectric point of this calcium carbonate has been measured at $\text{pH} = 9.6$.³⁷

Sample Preparation

For both adsorption isotherm determination and viscosity measurements, calcium carbonate particles were suspended in polymer solutions and the sample was sonicated for 2 min with a Sonimasse high power ultrasound device. After a first equilibration time, the pH was set at 11 by addition of a small volume of concentrated sodium hydroxide and an equilibration time of 18 h at 20°C was allowed to elapse for before measurements. The CaCO_3 content was 20 wt % for all measurements presented here, and the concentration of polymer was varied.

Polymer Adsorption Isotherm Determination

Equilibrated CaCO_3 suspensions were ultracentrifuged with a Beckman JA 21 centrifuge at 20°C and the supernatant was isolated and analyzed for the polymer content. The adsorbed amount $\Gamma(\text{mol}/\text{m}^2)$ was calculated from the difference of polymer concentrations before (C_i) and after (C_f) adsorption as

$$\Gamma = \frac{(C_i - C_f)V}{MA_{sp}} \quad (1)$$

where V is the solution volume, M is the CaCO_3 weight and A_{sp} is the particles specific area ($22 \text{ m}^2/\text{g}$). For nEO-S1, nEO-P1 and nEO-P2, the residual polymer concentration was measured by plasma ionization (Fison ARL 3520) analysis of the sulfur or phosphorous element at the Service Central d'Analyses of the CNRS (SCA-CNRS, BP 22, 69390 Vernaison). For nEO-OH, the carbon content of the solutions was analyzed for with a Doorman carbon analyser. Before this carbon analysis could be carried out, traces of soluble calcium carbonate (its solubility in water is 0.015 g/L) were removed by adding gaseous hydrogen chloride to the solution and eliminating the formed carbon dioxide by a nitrogen flow.

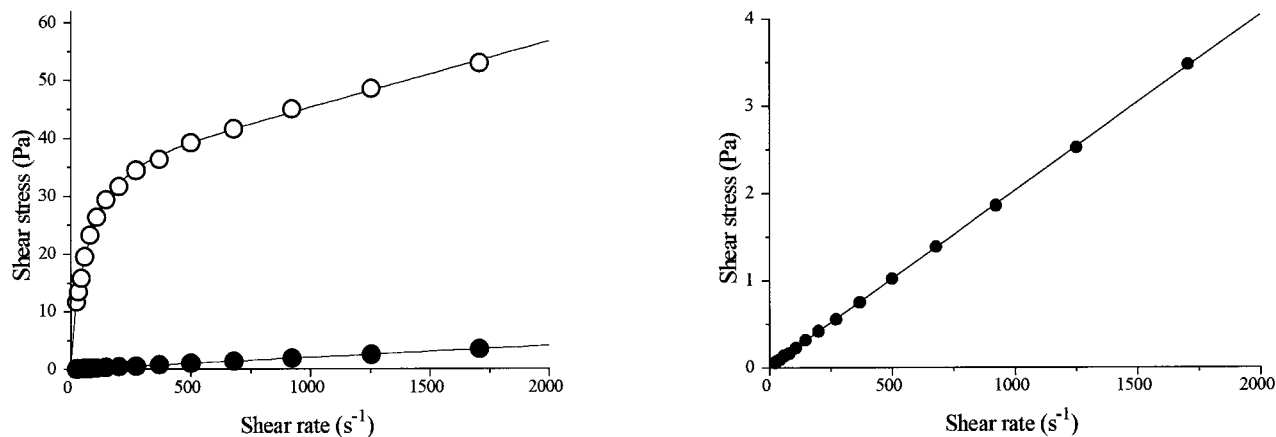


Figure 3 Rheological behavior of aqueous suspensions of CaCO_3 particles without (○) and in the presence of 0.83 mmol/L (2.1 g/L) 50EO-P2 polymer (●). The same stress vs. shear rate data are shown with two different shear stress scales on the left and right. The solid lines are guides for the eyes only.

Viscosity Measurements

The viscosities of calcium carbonate suspensions in the presence of various concentrations of nEO-X polymers were measured as a function of shear rate with a Rheomat RM30 (Contraves) rheometer. The stress was obtained from measurements of the torque when a fixed shear rate was applied between two coaxial stainless steel cylinders. The suspension viscosity was calculated as the stress to shear rate ratio. Applied shear rates were varied from 20 to 1708 s^{-1} .

RESULTS AND DISCUSSION

Adsorption of 50EO-P2 and Subsequent Viscosity Reduction of CaCO_3 Dispersions

The main features of a long chain di-phosphonate polymer (50EO-P2) are first presented before the discussion of the influence of the molecular parameters (polymerization degree and type of chain-end group). This polymer is one of the most efficient of the present series in lowering the viscosity of CaCO_3 particle suspensions.

The rheological behavior of the polymer-free aqueous suspension of calcium carbonate (20 wt % CaCO_3 , pH = 11) is that of a nonstabilized colloidal suspension. Shear thinning is the main characteristic, and the behavior at low shear rates is close to that of the Bingham model³⁸ (Fig. 3). The presence of a yield stress cannot be ascertained in the present work because of the difficulties encountered in measuring a stress thresh-

old with a rheometer working at constant applied shear rate. Shear thinning results from the disruption of flocculated structures by shear. The particle–particle contacts that have been broken as the shear rate was increased could be restored when the shear was cut off or as the shear rate was decreased. Indeed, no significant hysteresis was observed in the rheological behavior (in the shear rate range scanned, $\dot{\gamma} < 1708 \text{ s}^{-1}$). The shear thinning behavior is thus clearly associated with a poor colloidal stability of CaCO_3 particles.

Adsorption of the polymer 50EO-P2 at the particle surface provides a steric barrier acting against particle aggregation and changes the shear thinning rheological behavior into a Newtonian behavior with a low viscosity (Fig. 3). The control of suspension rheology by adsorbed polymers and the close relation of rheological behavior with interparticle interactions have been demonstrated in the case of suspensions of polymer particles (latexes).^{39–43} This is successfully applied to inorganic particle suspensions in the present work.

Starting from a polymer-free suspension, the rheological behavior turns progressively from Bingham to Newtonian as the polymer concentration is increased. For a discussion of the rheological data as a function of polymer type or concentration, the viscosity at the largest measured shear rate (1708 s^{-1}) was calculated as the stress to shear rate ratio. This is the correct definition for Newtonian flow but it was also applied to non-Newtonian flows because it allows a direct visualization of the effect of polymer concentration or

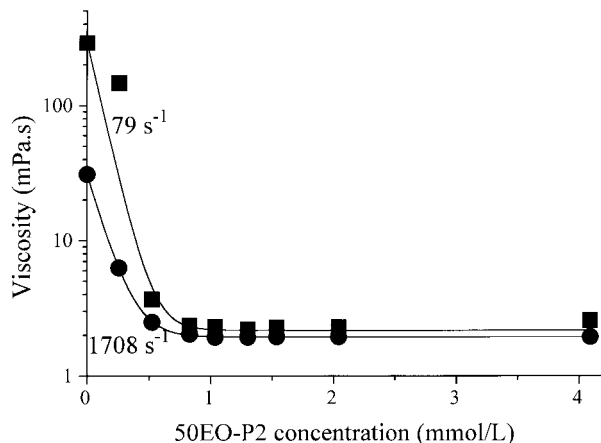


Figure 4 Viscosities of 20 wt % CaCO_3 particle aqueous suspensions at 79 s^{-1} (■) and 1708 s^{-1} (●) shear rates as a function of 50EO-P2 polymer concentration.

comparisons of the effects of different polymers, avoiding a complete analysis of the rheological behavior for each sample.

The viscosity decreases sharply as polymer is added and reaches a nearly constant value of $2 \text{ mPa} \cdot \text{s}$ above 2 mmol/L polymer concentration (Fig. 4). This viscosity value is very low because it is only twice that of pure water; low concentrations of polymer are required to reduce the viscosity of a 20 wt % CaCO_3 suspension to this level. This exceptional efficiency is the result of the molecular architecture of the polymer where the hydrophilic polymer part is long enough for efficient steric stabilization and the di-phosphonate group at the chain end has a strong affinity for the particle surface. The adsorption isotherm (Fig. 5) provides useful information on the adsorption-free energy and on the adsorption mechanism.

The adsorbed amount per unit area, Γ , increases steeply as the volume concentration increases but does not reach a plateau at high volume concentrations. Adsorption increases slightly but continuously for concentrations in the aqueous phase C_f larger than 0.3 mmol/L ($\Gamma > 0.2 \mu\text{mol/m}^2$). Two adsorption regimes can thus be distinguished. At low concentrations ($C_f < 0.3 \text{ mmol/L}$), strong adsorption of the di-phosphonate groups on surface sites occurs, the polymer part that is attached to the di-phosphonate group does not influence the adsorption process. At higher concentrations ($C_f > 0.3 \text{ mmol/L}$), the adsorbed amount Γ reaches such a value that the adsorbed macromolecules cannot be considered as dilute. Thus, excluded volume interactions between polymer coils swollen in a good solvent at

the surface inhibit further adsorption. These two concentration regimes that are observed experimentally correspond to the “mushroom” (dilute) and “brush” (semidilute) regimes as described in the Introduction section. The transition is found at a surface coverage ranging between 0.15 and $0.2 \mu\text{mol/m}^2$, for which the surface area per macromolecule is between 8.3 and 11.0 nm^2 . This is not a well-defined transition, however, and only orders of magnitude are considered in the following. Assuming that the polymer coil adsorbed at the surface has the same radius of gyration as in bulk aqueous solution, the surface area per unperturbed adsorbed macromolecule can be calculated. Thus, the radius of gyration of polyethylene oxide in water depends on its molar mass according to the power law⁴⁴

$$R_g = 0.0215M_w^{0.583} \text{ nm} \quad (2)$$

R_g is then 1.91 nm for 50EO-P2, which gives an area $a = \pi R_g^2 = 11.5 \text{ nm}^2$, close to the experimental surface coverage at the transition. Moreover, the full shape of the adsorption isotherm compares qualitatively well with the theoretical calculations of hindered adsorption of end functional polymers by Ligoure and Leibler.⁴⁵ Below the surface coverage of transition, some parts of the calcium carbonate surface remain bare, while the surface is completely covered by a polymer layer for surface coverages above the transition.

For a 20 wt % CaCO_3 dispersion, the crossover from isolated (dilute) adsorbed macromolecules to the brush regime corresponds to a total polymer concentration (residual + adsorbed) of the order

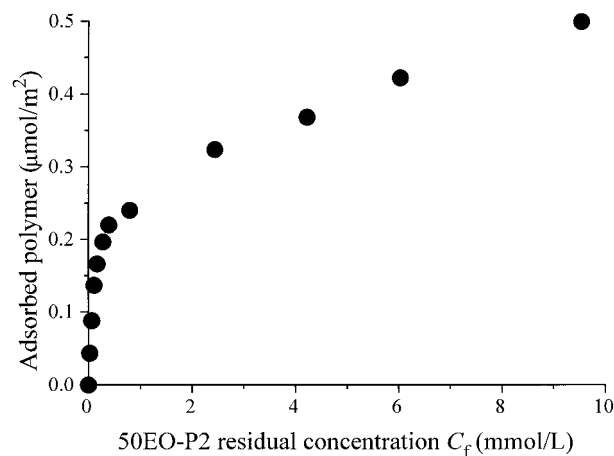


Figure 5 Adsorption isotherm of the 50EO-P2 polymer on CaCO_3 particle surface.

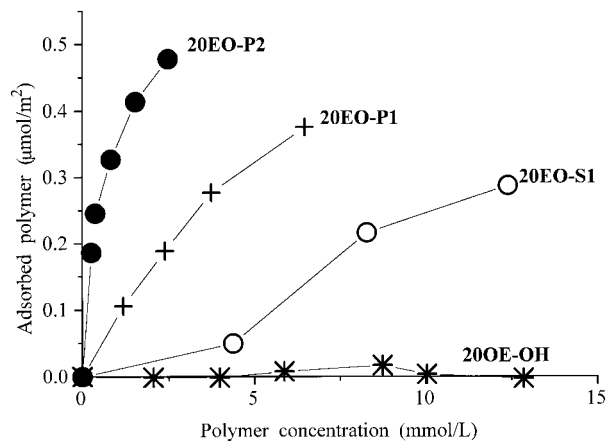


Figure 6 Adsorption isotherms of functional polymers on CaCO_3 .

of 1 mmol/L. This is the polymer concentration above which the suspension viscosity stabilizes (Fig. 3). We, thus, conclude that efficient steric stabilization and fluidization of a suspension of CaCO_3 particles can be obtained by polymer adsorption when the full surface is covered with polymer. Once the surface is completely covered, further polymer adsorption does not produce any additional effect. The minimum amount of adsorbed polymer that is required corresponds to the crossover concentration between the “mushroom” and “brush” regimes.

Influence of the Type of Chain End Group

Different chain ends with different affinities for calcium carbonate were studied, namely hydroxy-, sulfonate, carboxylate, mono-, and di-phosphonate. The hydroxy terminated polymer is simple polyethylene oxide (PEO) and was studied as a reference nonadsorbing polymer. It was indeed experimentally verified that low molecular weight PEO could not adsorb on calcium carbonate particles and that the viscosity of the suspensions was not affected by the presence of polymer.

The adsorption isotherms of 20EO-S1, 20EO-P1, and 20EO-P2 have been measured in the low polymer concentration domain where the influence of the polymer chain is weak, so that the influence of the functional chain end could be observed. Adsorption-free energy, which is qualitatively related to the slope of the curves of Figure 6, increases in the order $20\text{EO-S1} < 20\text{EO-P1} \ll 20\text{EO-P2}$. The same order was found for the efficiency of viscosity reduction (Fig. 7). The con-

sequences of a low adsorption-free energy are of two types. First, the full coverage of the particles' surface (brush regime) requires the use of a larger total polymer concentration because the adsorbed amount is in equilibrium with a larger concentration in the aqueous solution phase. Secondly, the constant viscosity value of the suspension in the brush regime is higher. This second observation of importance appears in contradiction with the simple ideas given in the preceding part of this article. Strong anchoring of the polymer seems to be a requirement for attaining a large viscosity lowering. We do not believe that shear could cause any desorption of the polymer by a mechanical pull-out mechanism. Experimental observations reviewed by Klein⁴⁶ show an enhancement of interparticle repulsions under shear.⁴⁷ The origin of this effect may more likely be caused by an incomplete deaggregation of the CaCO_3 flocculated clusters when the adsorption-free energy is too low. The calcium carbonate surface may be heterogeneous and some crystallographic faces may be poor sites for adsorption. In this case, only functional polymers having a strong affinity for these kinds of crystallographic faces can adsorb and provide a fluidifying effect. In the absence of adsorption on such faces, some parts of the particle surfaces remain completely bare, and particle sticking may occur. The area of such crystallographic faces may be small as compared to the total area so that the extent of their coverage cannot be observed in adsorption isotherms, but their influence is determinant. According to this hypothesis, efficient viscosity reduction requires a really full coverage of all the particle surfaces.

The adsorption follows qualitatively the com-

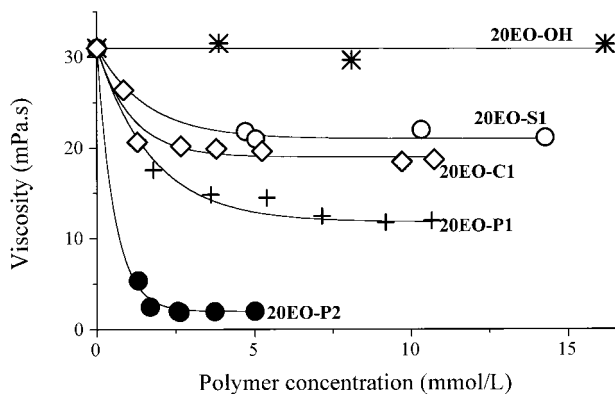


Figure 7 Viscosity of a 20% dispersion of CaCO_3 at 1708 s^{-1} shear rate as a function of the concentration of added functional polymer.

plexing properties of carboxylate, sulfonate, and phosphonate groups towards calcium ions. Thus, the complexing agents containing phosphorus (the P—O group) such as phosphonates, phosphates, or phosphine oxides are well known, especially for alkaline-earth and transition metal ions. The large equilibrium calcium complexation constants of mono-phosphonate and various di-phosphonates including some amino-bis(methylene phosphonates) have been reported.^{48–60} Thus, the mono-phosphonate adsorption is stronger than that of the carboxylate and sulfonate. The adsorption of the di-phosphonate is obviously larger than that of the mono-phosphonate because adsorption of one phosphonate group of a di-phosphonate molecule brings the second phosphonate group close to the surface. There is a favorable entropic contribution for the adsorption of multifunctional molecules that is similar to the “chelate effect” for complexes in solution. The relationship between adsorption and complexing properties towards Ca^{2+} ions is a guide for the design of efficient polymers but remains qualitative. The strength of the chemical bond between the surface site and the complexing molecule that adsorbs is only one of the parameters that determine the adsorption-free energy. The geometrical matching of the adsorbing molecules into the surface sites is also important.^{61,62} This depends on the types of crystallographic faces exposed to the solvent—thus, on the surface heterogeneity. In any case, adsorption may be considered as a substitution of carbonate ions for phosphonate ions at the CaCO_3 surface.^{6,7}

Influence of the Polymer Molecular Weight

The length of the polymer chain influences both the adsorption process and the colloidal stability of the suspension. Thus, where the surface is too crowded with adsorbed polymer chains, further adsorption is hindered. The influence of the polymeric nature of the molecules is a levelling of the adsorption at high coverages because of polymer–polymer interactions in the adsorbed layer. Because the radius of the adsorbed polymer coil is equal to the gyration radius found in bulk solution, the thickness of the adsorbed layer is larger for higher molecular weight polymers. Efficient steric stabilization of the particles is obtained when the polymer layer thickness exceeds the range of the attractive interparticle forces that would cause flocculation.

For the di-phosphonate polymers, the adsorption isotherms (Fig. 8) clearly show the adsorption hindrance phenomenon due to the polymer excluded volume effect. Thus, for all molecular weights studied, adsorption isotherms are identical in the dilute regime. All the compounds having the same di-phosphonate chain end adsorb with the same adsorption-free energy. But polymer–polymer interactions arise at lower surface coverage for larger molecular weight polymers. It has been stated in the preceding section that the transition concentration at which the dilute regime with a steeply increasing adsorption turns to a hindered adsorption regime corresponds to the onset of full surface coverage by the polymer coils. At this transition concentration, the adsorbed amount is thus

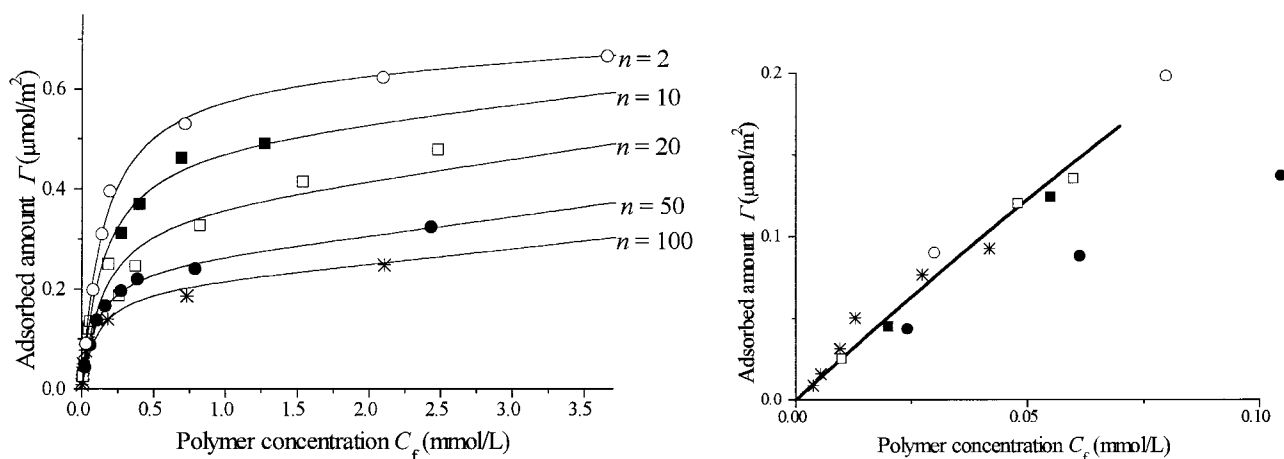


Figure 8 Adsorption isotherms of nEO-P2 functional polymers as a function of the degree of polymerization n . (\circ) $n = 2$; (\blacksquare) $n = 10$; (\square) $n = 20$; (\bullet) $n = 50$; ($*$) $n = 100$. An expansion of the low polymer concentration domain is shown on the right part of the figure. The solid lines are guides for the eyes only.

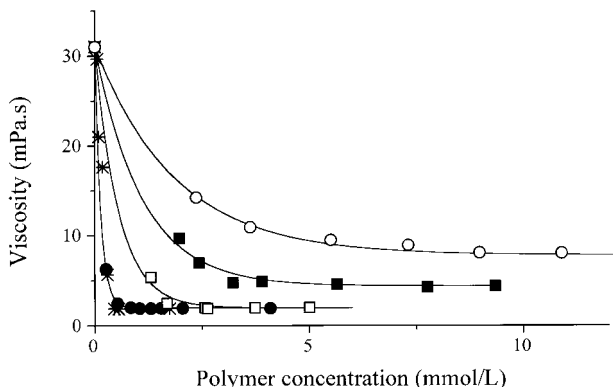


Figure 9 Viscosity of a 20% dispersion of CaCO_3 at 1708 s^{-1} shear rate as a function of the concentration of nEO-P2 polymers of varying degree of polymerization n . (\circ) $n = 2$; (\blacksquare) $n = 10$; (\square) $n = 20$; (\bullet) $n = 50$; ($*$) $n = 100$. The solid lines are guides for the eyes only.

$$\Gamma_{\text{trans}} = \frac{1}{N_{\text{Av}}\pi R_g^2} \quad (3)$$

where the radius of gyration R_g is given by eq. (2). It has also been noticed in that the suspension viscosity lowering ceases when full coverage of the surface by the polymer is reached. The viscosity data (Fig. 9) and the adsorption isotherm each allow us to determine the adsorbed amount at the transition. Equation (2) does not apply to low molecular weight polymers (2EO-P2 and 10EO-P2). For $n \geq 20$, the predicted adsorbed amounts at the transition and the experimental ones obtained from the adsorption isotherm or from the viscosity measurements (Table I) compare well for different polymer molar weights. This good correlation for a series of polymers supports the ideas presented above.

As stated previously, the two adsorption regimes are the dilute (mushroom) regime where polymer chains are unperturbed at the surface and the brush regime where polymer chains are

densely packed at the surface and constrained to stretch perpendicular to the surface. The free energy cost of this conformational change is the thermodynamic origin of the levelling of the adsorption isotherm. Thus, there is no plateau in the adsorption isotherm as would be observed with small molecules but a weak increase of the adsorbed amount as the polymer concentration in the solution increases. The occurrence of a plateau in adsorption isotherms generally indicates that all surface sites are occupied by adsorbed molecules. This is not the case here, because the adsorbed amount in the high concentration regime depends on the polymer molar mass.

The viscosity of 20 wt % CaCO_3 aqueous suspensions at 1708 s^{-1} shear rate (Fig. 9) decreases as a function of the concentration of added polymer and reaches a constant value for polymer concentrations larger than 1 to 2 g/L, depending on the type of polymer. A constant viscosity value is reached when the particle surface is completely covered with adsorbed polymer as already discussed. Its value depends on the polymer molecular weight in a simple way: a viscosity of $2 \text{ mPa} \cdot \text{s}$ can be obtained when the polymer chain is long enough (more than 20 ethylene oxide units). In this case, the steric stabilization by the polymer is very efficient because the thickness of the polymer layer exceeds the range of the attractive interactions between particles. This thickness is equal to the radius of gyration of PEO having 20 EO units (1.1 nm). The constant viscosity at high concentration decreases as a function of the polymer molecular weight for $n < 20$, and there is a slight but persistent decrease of viscosity in the whole concentration domain for 10EO-P2 and more significantly for 2EO-P2. These two compounds of low molecular weight do not behave like true polymers.

For polymers that adsorb less strongly such as the nEO-P1, the variation of adsorption isotherms

Table I Adsorbed Polymer Amount per Unit Surface Area Γ_{trans} ($\mu\text{mol}/\text{m}^2$) at the Transition between the Dilute and the Brush Regime as Obtained from the Radius of Gyration (Theory), from the Adsorption Isotherm, and from Viscosity Data, as a Function of the Molecular Weight of the Di-Phosphonate Polymers

	Radius of Gyration R_g (nm)	Γ_{trans} from Theory [eq. (3)]	Γ_{trans} from the Adsorption Isotherm	Γ_{trans} from Viscosity Data
20EO-P2	1.12	0.42	0.3–0.4	0.35
50EO-P2	1.91	0.145	0.15–0.2	0.14
100EO-P2	2.86	0.065	0.07–0.10	0.07

and viscosity data with molecular weight is very weak and the viscosity lowering at high polymer concentration is moderate. The viscosity at high polymer concentration is not perfectly constant and reaches only $15 \text{ mPa} \cdot \text{s}$ at 1708 s^{-1} shear rate for 50EO-P1. Moreover, a yield stress is always present in the rheological behavior, even at high polymer concentrations. From these observations, it is clear that a strong adsorption is a prerequisite for particle stabilization with chain end-functionalized polymers.

GENERAL DISCUSSION

The use of polymers with a di-block architecture allows one to distinguish the different contributions of the adsorbing groups on one hand and hydrophilic polymer on the other hand. A strong adsorption-free energy is an absolute requirement for obtaining a full coverage of the surface. A weak adsorption-free energy cannot be compensated by a larger polymer concentration. The present studies were carried out at $\text{pH} = 11$, above the isoelectric point of calcium carbonate.³⁷ The particle surface is thus negatively charged and the adsorption of the anionic di-phosphonate group is strong in spite of an unfavorable electrostatic effect. The driving force for adsorption is thus a true binding to the surface (surface complexation), this is not an electrostatic adsorption. It is likely that strong adsorption would occur at any pH and ionic strength.

Another advantage of the strong adsorption is that the residual polymer concentration in the solution is low. For example, the fraction of adsorbed 50EO-P2 polymer for a 20 wt % CaCO_3 suspension is close to 90% in the dilute regime of adsorption (Fig. 10). There is an obvious economic benefit because the major part of the added polymer is active at the particle surface. But a low concentration of polymer in solution is also important for colloidal stabilization because a high osmotic pressure is kept in the aqueous phase. The presence of a high concentration of free polymer in solution would lower the osmotic pressure and may cause depletion flocculation or shrinkage of the polymer layer onto the surface.⁶³

The type of the polymer part and its length can be selected at will because of the di-block architecture. The polymer is chosen such that the solvent is a good solvent for the polymer. The nonionic nature of PEO also provides some versatility to these polymers because the steric stabilization is

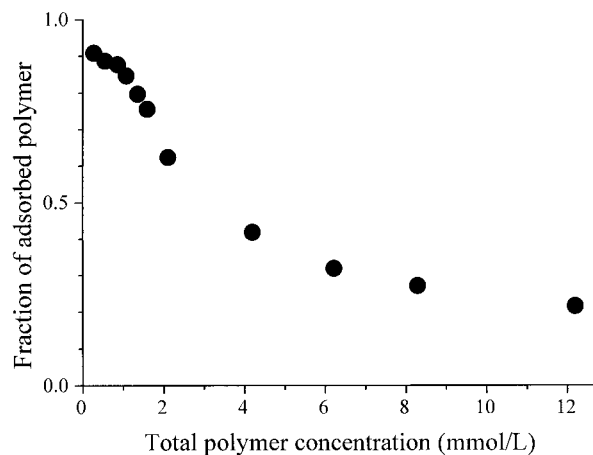


Figure 10 Mole fraction of 50EO-P2 adsorbed polymer for a 20 wt % CaCO_3 suspension is presented as a function of total concentration (adsorbed + residual).

expected to be independent of the ionic strength. On the contrary, stabilization by a polyelectrolyte such as sodium polyacrylate^{6,7} vanishes at high ionic strength because the electrostatic interactions involved in the stabilization mechanism are screened out and the adsorbed polymer collapses onto the surface. For chain end-functional PEO, particle destabilization by added electrolyte would require very large salt concentrations where the solvent (brine) turns to theta or poor solvent conditions for PEO (salting-out).

The longer the polymer chain, the smaller the adsorbed amount, Γ , required for attaining full coverage of the surface. But this is only true when the surface excess Γ is expressed in mol/m^2 units. For a practical point of view, the amount of added polymer is more often expressed in weight units. If the weight of added polymer per weight of calcium carbonate is considered, then the amount of polymer required for reaching a constant low viscosity of a 20 wt % CaCO_3 suspension is found approximately independent of the polymer molecular weight (Fig. 11). This can be simply understood as follows. The adsorbed amount at the dilute to brush regime transition Γ_{trans} is given by eq. (3) in mol/m^2 units. The same quantity in weight of polymer per unit area is $\Gamma_{\text{trans}} M_w$. Substituting the exponent 0.583 in the expression of the radius of gyration [eq. (2)] by the rounded value of $1/2$ as $R_g = kM_w^{0.5}$, the adsorbed polymer weight per unit area is then $\Gamma_{\text{trans}} M_w = 1/N_{\text{Av}} \pi k^2$, independent of M_w . This adsorbed amount is the major part of the added polymer because the fraction of adsorbed polymer is close to 1 (Fig. 10).

The main advantage of the di-block architec-

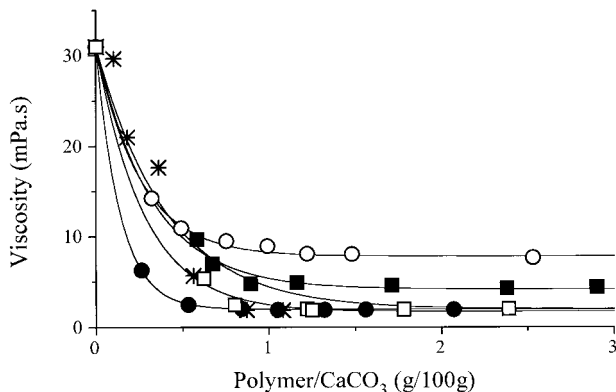


Figure 11 Viscosity data for the nEO-P2 polymers as in Fig. 9, plotted as a function of the polymer-to- CaCO_3 weight ratio. (○) $n = 2$; (■) $n = 10$; (□) $n = 20$; (●) $n = 50$; (*) $n = 100$.

ture of the polymers is their ability to lower the viscosity of inorganic CaCO_3 suspensions quite efficiently upon addition of small quantities. The “brush” structure of the adsorbed layer is the origin of this efficiency: direct force measurements between surfaces covered by polymer brushes have shown the larger range of the steric repulsion with respect to that of a classical adsorbed polymer layer (with adsorbed trains and protruding loops and tails).^{64–68}

CONCLUSIONS

Polymers having a functional group at one of their chain end, which can strongly adsorb on the surface of particles are very efficient for steric stabilization of colloidal suspensions. The direct consequence of the increased colloidal stability is the fluidization of concentrated slurries of flocculated particles. With the di-phosphonate functional group, viscosities as low as 2 mPa·s for 20 wt % calcium carbonate suspensions in water could be obtained. Low levels of dispersing agent are required because the largest part of the added polymer adsorbs onto the particle surface, achieving a complete coverage of the surface at the dilute (“mushroom”) to “brush” transition predicted by the theoreticians. This property is obtained because the di-block architecture of the polymers imposes the structure of the adsorbed polymer layer as a brush.

On another hand, the advantage of building a polymer with two independent blocks having their own functionality is that a clear control of the

properties at the stage of the polymer synthesis is possible. Thus, the adsorption-free energy and the thickness of the adsorbed layer (the strength and range of the steric stabilization) can be varied independently. Easy studies of the structure–properties relationships can be carried out, but this also allows the design of polymers with specific properties, using the concepts of molecular recognition at the surfaces.

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