Binding of Polymers to Calcite Crystals in Water: Characterization by Isothermal Titration Calorimetry

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The interaction of double hydrophilic block copolymers with calcite crystals is studied by isothermal titration calorimetry. These polymers are known to possess high activity as crystal growth modifiers for inorganic substances. Different titration protocols are used in order to decompose the total heat flow into several components arising from different physicochemical processes. This allows us to distinguish the effects due to the hydration of each of the polymer blocks, the interaction of the polymer with the ions, and the adsorption of the polymer to the exposed calcite surfaces. The observed concentration dependence of the heat of adsorption is consistent with a simple Langmuir type adsorption model, which leads to the numerical values -1.77 J/m^2 and 28 mM^{-1} for the surface adsorption enthalpy and the equilibrium constant, respectively. The titration measurements reveal the existence of a strongly endothermic process, which we believe to arise from the binding of the polymer to a further solution species, presumably very small amorphous calcium carbonate clusters. This together with other thermodynamic data indicates that the structure of water plays an important, currently not fully recognized role in the control of mineralization processes.

Introduction

Functional, water-soluble polymers with the ability to bind ions and crystals play a major role as scale inhibitors.[1,2] These polymers are used on a daily basis in detergent formulations but are also applied in seawater desalination, in oil drilling, or for the protection of pipe systems. After polyphosphates were banned because of environmental reasons, polycarboxylates such as poly-(acrylic-*co*-maleic acid) or polyaspartate have been commonly used but showed only a moderate performance.

Recently, new types of block copolymers, namely, double hydrophilic block copolymers (DHBCs),[3] have been developed which exhibit a much stronger influence on crystallization processes. These block copolymers are composed of a short mineral binding block, which interacts strongly with the crystal surfaces, and another hydrophilic moiety, which interacts only weakly with ions or crystal faces and, thus, promotes dissolution even under high ionic strength conditions. For CaCO$_3$, these DHBCs were found to exhibit a mass efficiency for scale inhibition, which is up to a factor of 10–15 larger than for standard systems used in detergent formulations.[4] In addition, studies on the properties of water–poly(ethylene oxide) systems demonstrated the ability of those polymers to modify water structure as well.[5]

DHBCs also strongly modify the morphology of growing crystals in an interesting manner. Indeed, in the presence of such polymers, the nucleated crystals may adopt a variety of shapes. The interacting part of the DHBC is oligomeric (6–20 functional groups) and can be selected or designed in such a way that it specifically adsorbs to a certain crystal face. The feasibility of this approach has been previously demonstrated by employing different DHBCs to control the morphologies of various biominerals, including calcium carbonate,[6] calcium phosphate,[7] and barium sulfate.[8] These morphological experiments already indicated that the interaction of the polymers with the crystal surfaces competes with a variety of additional interactions, namely, crystal/water, polymer/water, water/ion, and polymer/ion interactions. In addition, special DHBCs were found to change fundamental water properties such as melting behavior, ice structure, viscosity, and density.[9]

In the present article, we study the interactions of DHBCs with calcite crystals using isothermal titration calorimetry (ITC), a highly sensitive calorimetric technique, which was previously applied to other self-organization processes such as micelle formation,[10] adsorption of small amphiphilic molecules onto vesicles,[11] and anchoring of polymers into lipid membranes.[12]

ITC measures the exchanged heat arising from the addition of the DHBC solution to the calcite dispersion. Using different titration protocols, we are able to decompose the total heat flow into several components corresponding to different physicochemical processes. One of these processes is identified with the adsorption of the polymers onto the crystal surfaces. The latter process is found to be exothermic and to agree quantitatively with a simple, Langmuir type adsorption model.

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Scheme 1. Reaction Scheme for the Synthesis of (i) the Polymer P_{OH} from PEO-*b*-PB and (ii) the Polymer P_{Phos} from P_{OH}

PEO-b-PB P_{OH} P_{Phos}
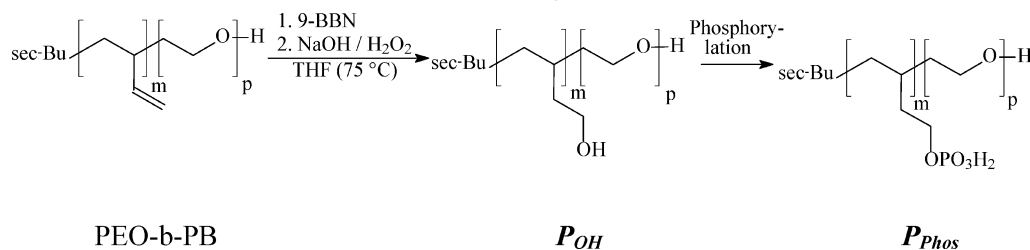
Table 1. Description, Molecular Weight, and Concentration of the Three Polymer Species Used in the Experiments

polymer	description; degree of phosphorylation	molecular weight (g/mol)	concentration of added polymer, C_P^0
P_{OH}	PEO_{84}-*b*-$PHEE_{13}$; 0%	4690	1 g/L (2.132×10^{-4} M)
P_{Phos}	PEO_{84}-*b*-$PHEE_{13}$; 40%	5106	1 g/L (1.958×10^{-4} M)
PEO	PEG-5000 (PEO_{113}); −	5000	1 g/L (2.0×10^{-4} M)

The article is organized as follows. First, we describe the experimental procedures used to prepare the DHBCs and the calcite dispersion and to perform the ITC measurements. Second, we introduce a Langmuir type model for the polymer adsorption on the calcite crystals, which expresses the exchanged heat in terms of the adsorption enthalpy per polymer and of the various concentrations. In the main section, we discuss our ITC results for (i) polymer hydration, (ii) a mixture of polymer solution and calcite dispersion, (iii) polymer adsorption on large calcite crystals, (iv) polymer/ion interaction, and (v) a mixture of polymer solution with a centrifuged calcite dispersion. The analysis of these different ITC measurements strongly indicates that in addition to calcium ions and calcite crystals, the calcite dispersion contains another species, which we postulate to consist of small aggregates or clusters.

Experimental Section

Polymer Synthesis and Purification. Poly(ethylene oxide)-*block*-poly(1,4-butadiene) (PEO-*b*-PB) was synthesized according to ref 13 and transferred into poly(ethylene oxide)-*block*-poly(hydroxyethyl ethylene) (PEO-*b*-PHEE) via quantitative hydroboration with 9-bora-bicyclo[3.3.1]nonan (9-BBN) according to Ramakrishnan.[14] The crude product was cleaned by exhaustive ultrafiltration (membrane MWCO 1 kDa, Millipore) until the signals of the 1,5-cyclooctane-diol side product were absent in ^{13}C NMR. The product was characterized by ^{1}H NMR and gel permeation chromatography. The phosphorylation of the hydroxyl side groups and product cleaning by 2-day dialysis were performed as described by Kaluzynski et al.[15] and Rudloff et al.[16] The degree of phosphorylation was determined by quantitative ^{31}P NMR spectroscopy. Scheme 1 displays the chemical structure of the different block copolymers used here.

The hydroxylation was performed with practically complete conversion, whereas phosphorylation occurs only with a conversion of about 40%. This means that the phosphorylated polymer carries, on the average, 6 phosphate groups and 7 hydroxyl groups. The data of those polymers are summarized in Table 1. At the conditions of the measurements and for polymer concentrations such as those used, the phosphate groups are typically deprotonated and carry one negative electric charge. It is also unlikely that at such low concentrations aggregation of the

polymer molecules occurs. This is confirmed by both static and dynamic light scattering measurements, which are however not reported here. The pHs of the used polymer solutions were measured to be slightly basic, that is, around 8 (most likely due to minute traces of NaOH from the polymer synthesis). This value is close to the pH of the calcite solution (8.3). Therefore, acid/base reactions or partial dissolution of calcite are expected to be suppressed.

Calcite Preparation. $CaCO_3$ crystals were prepared by a slow crystallization process following the method of Kitano et al.[17] Briefly, a supersaturated solution of $CaCO_3$ was prepared by bubbling CO_2 gas through a solution of 5 g of $CaCO_3$ in 4 L of pure water for 60 min. The $CaCO_3$ was subsequently filtered off. Then, to dissolve the remaining $CaCO_3$ particles, CO_2 was bubbled through for another 30 min. The solution was left in unsealed vessels, carbon dioxide was formed, and precipitation of $CaCO_3$ crystals with well-defined morphology and reproducible size and surface area[16] occurred normally within 1 or 2 days. In general, the magnitude of the corresponding surface area can be determined only approximately. Direct inspection of the crystals via optical microscopy on large sample sets indicates that the average volume of the crystals is about 10 μm × 10 μm × 5 μm and the average surface is about 400 μm^2. Using this average crystal volume together with the density of calcite, which is 2.71 g/cm^3,[18] and the value of the starting calcium concentration, one obtains the estimate 1.5 m^2/L for the available crystal surface area per solution volume. Note that it has been tacitly assumed here that all calcium carbonate is incorporated into the calcite crystals because of the low solubility product of calcite.

ITC Experiments. The titration measurements were performed with the VP-ITC calorimeter produced by MicroCal Inc. (Northampton, MA). The volume of the working cell is 1.442 mL. Analysis and data fit procedures were performed with MicroCal Origin software.

The polymer solutions were injected into suspensions of calcite crystals. We assume that one of the interactions taking place is binding of polymer molecules to available adsorption sites on the surface of the crystals. Because of stirring in the working cell, we ignored possible sedimentation of the crystals.

ITC measures the heat flow associated with mixing two solutions, in our case a polymer solution and a dispersion of calcite crystals. The calorimeter has two cells, the working cell and the referent cell. The latter is filled with the solution medium, which is water in our experiments. Small aliquots of polymer are then added to the solution in the working cell. The latter cell is constantly stirred with a stirring rate of 480 rpm. The instrument (an adiabatic calorimeter) measures heat flow by compensating the temperature difference between the two cells. In this way, each ITC measurement leads to a group of injection peaks at (usually) evenly spaced time intervals (an example of an ITC measurement is presented in the insert of Figure 2, see legend for details). A constant baseline is subtracted from the data in order to set the no-injection signal equal to zero. The integration of the injection peaks over time provides the heat released or absorbed for each injection, that is, associated with the addition of one aliquot of polymer solution to the crystal dispersion. All measurements were performed at room temperature, that is, at 25 °C or 298 K.

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Langmuir Type Model for Polymer Binding

The heat released or absorbed in the working cell can arise from different physicochemical processes, such as the chemical interaction of the polymer molecule with the surface sites available at the crystal faces and/or the removal or "liberation" of water molecules previously bound to the crystal surface. The process of main interest is the adsorption of the polymer molecules onto the crystal surfaces. The latter surfaces can be viewed as two-dimensional lattices of adsorption sites. When the adsorption/desorption process is viewed as a chemical reaction, one has two species, namely, the free (or unoccupied) surface site S and the polymer P, which react according to

$$S + P \leftrightharpoons SP$$
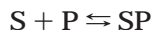
and, thus, form an SP complex consisting of one polymer bound to one surface site. The polymer concentration in the working cell will be denoted by C_P, the concentration of free surface area by C_S^f, and the concentration of occupied surface area by C_{SP} (note that the units of C_S^f and C_{SP} are m²/L). Because we do not know the surface area occupied by a single adsorbed polymer, we chose to work directly with crystal surface area per volume of solution. The equilibrium state of the interaction process can be described by an association equilibrium constant

$$K = \frac{C_{SP}}{C_S^f C_P} \tag{1}$$

At the same time, the total concentration of crystal sites is given by

$$C_S = C_{SP} + C_S^f \tag{2}$$

where C_S is the total area of crystal surface. In general, C_P should be the concentration of free (not bound) polymer. Written in this way, the model represents a Langmuir type adsorption, for which the concentration of bound polymer is assumed to be negligible compared to the free polymer concentration (this will be a posteriori justified by the experimental data); then the free polymer concentration C_P^f can be approximately equated to the total available polymer in the cell, $C_P^f \approx C_P$. (More generally, one should replace C_P in eq 1 by C_P^f, which depends on C_{SP}). Expressing C_S^f from eq 2 and introducing it in eq 1 leads to the simple relation

$$C_{SP} = \frac{K C_S C_P}{1 + K C_P} \tag{3}$$

for the concentration of occupied surface area. In the course of the measurements, C_S and C_P are known variables. C_S stays approximately constant (except for small dilution effects which are accounted for). C_P is increased by consecutive injections of polymer. The change δC_{SP} in the concentration of occupied surface area is obtained by the first derivative of eq 3 which implies

$$\delta C_{SP} = \frac{K C_S}{(1 + K C_P)^2} \delta C_P \tag{4}$$

where δC_P is the change in the total polymer concentration due to a single injection. The released heat δh from a single injection is proportional to the additional surface area δC_{SP} occupied by the polymer,

$$\delta h = \delta C_{SP} V \Delta H \tag{5}$$

where V is the current volume of solution in the calorimeter cell and ΔH is the "surface" enthalpy of this interaction ΔH (the latter has units of J/m²). The units of δh are joules. To be able to compare measurements performed with different concentrations of the polymer solution and crystal dispersions, we will rescale δh by the moles of injected polymer and define

$$\delta \bar{h} = \frac{\delta C_{SP} V \Delta H}{V_{inj} C_P^0} \tag{6}$$

where V_{inj} is the volume of the injected aliquot (typically 10 μL), and C_P^0 is the concentration of the added solution of polymer.

Results

**Hydration of Polymers.** Two DHBCs based on PEO-*b*-PB were used, one with hydroxyl (P_{OH}) and one with phosphate units (P_{Phos}) in the side chain. To determine the influence of the solvating block alone, we also studied pure poly(ethylene oxide) (PEO) with M_w = 5000 g/mol and M_w/M_n < 1.03, where M_w and M_n are weight- and number-average molecular weights, respectively.

First, we injected different polymer solutions into water at room temperature. In this way, we measured the exchanged heat associated with the interactions between the polymer and water; see Figure 1. In this figure, the released or absorbed heat per injection, $\delta \bar{h}$, is plotted versus the polymer concentration in the working cell. Negative and positive values for the exchanged heat correspond to exothermic and endothermic processes, respectively.

The reference titration with PEO gives an exothermic signal ($\delta \bar{h} < 0$) corresponding to an exothermic heat of dilution or hydration energy. Inspection of Figure 1 shows that this signal stays essentially constant as one varies the polymer concentration. Indeed, the statistical error of these data is of the order of 4 kJ/mol and, thus, is comparable to the variance of the measured heat values. A heat of dilution, which is independent of the polymer concentration, is expected if the interaction between the polymer and water molecules is short-ranged and the water shells of different polymers do not "overlap".

The block copolymer with the hydroxylated segment, P_{OH}, shows qualitatively similar behavior (the size of the signal is similar to the one obtained when injecting water into water). As shown in Figure 1, the hydration of this block copolymer is somewhat less exothermic than the hydration of PEO. Since P_{OH} is composed of PEO and hydroxylated butadiene groups, this behavior implies that the hydroxylated butadiene dissolves in a slightly endothermic fashion.

The polymer P_{Phos}, on the other hand, shows a qualitatively different behavior. At low concentrations, the hydration of this block copolymer leads to an endothermic signal, which gradually changes to an exothermic one with increasing polymer concentration. The pH of the solution in the working cell remained essentially unchanged when the aliquots of polymer solution were added to this cell. Therefore, the trend in the signal cannot be attributed to pH variations. Since at higher concentrations the same polymer strongly modifies the density and viscosity of water,[9] we interpret the first, low concentration behavior in terms of a long-range restructuring of the water by the polymer, whereas the high concentration offset may
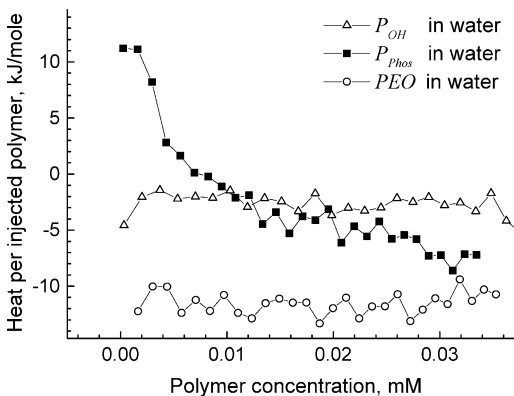
Figure 1. Concentration dependence of the heat per injected polymer, $\delta \bar{h}$, as defined in eq 6. The three different titration curves correspond to injecting three different polymers (PEO, P_{OH}, and P_{Phos}) into water at a temperature of 298 K.
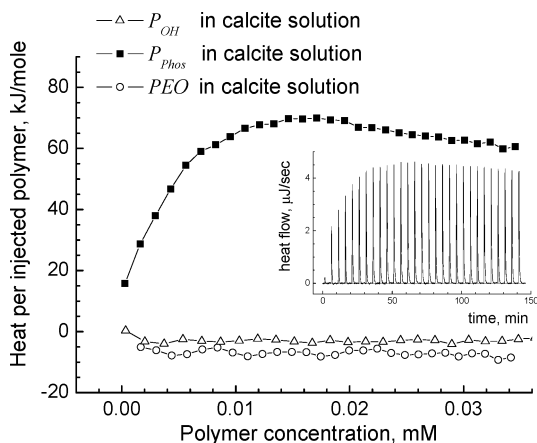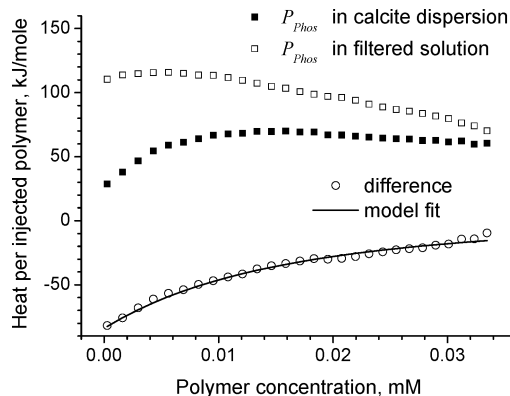

Figure 2. Concentration dependence of the heat per injected polymer, $\delta \bar{h}$, as defined in eq 6. The three different titration curves correspond to injecting three different polymers (PEO, P_{OH}, and P_{Phos}) into a dispersion of $CaCO_3$ at a temperature of 298 K. The insert presents the characteristic ITC peaks of injecting P_{Phos} in water (integration over time corresponds to the data displayed with black squares).

correspond to a short-ranged hydration of the polymer chain, as also observed for the PEO reference case.

Addition of Polymer Solution to Calcite Dispersion. In a second set of experiments, the same polymers were added to a $CaCO_3$ dispersion containing dispersed calcite crystals. As shown in Figure 2, the titration curves for both PEO and P_{OH} are very similar to those shown in Figure 1, which implies that the interaction between these polymers and the calcite is rather weak (the presence of calcite leads to a slightly lowered signal for PEO, which indicates that the hydration of $CaCO_3$ competes with the hydration of PEO). These data are consistent with those of previous experiments, which showed that these polymers do not induce scale inhibition or changes in the crystal growth morphology.

In contrast, when the phosphorylated polymer P_{Phos} is added to the calcite dispersion, we find a rather different behavior: the process is now strongly endothermic instead of exothermic and the exchanged heat is much larger.

Since the experiments are performed at constant pressure and temperature, the processes which occur must be characterized by a negative change in the Gibbs free energy: $\Delta G = \Delta H - T \Delta S < 0$, where T is the temperature and S is the entropy. For endothermic processes, this implies a large change in entropy $\Delta S > \Delta H/T > 0$. The latter is expected to have several contributions such as (i)

Figure 3. Concentration dependence of the heat per injected polymer P_{Phos} in the calcite dispersion (filled squares) and in the filtered calcite solution (open squares). The open circles represent the difference between these two measurements, which is attributed to the adsorption of polymer onto the crystal surface. The solid line is a theoretical fit according to eq 6 with fitting parameters $K = 31$ mM^{-1} and $\Delta H = -1.77$ J/m^2.

liberation of water molecules originally bound to the species present in the solutions and (ii) entropy of mixing arising from the addition of polymer solution to the calcite dispersion. As discussed further below, the concentration of calcium and carbonate ions is about 1.4×10^{-4} M. A rough estimate of the entropy of mixing per injected polymer is given by $k_B T C_{ions}/C_P$, which varies from 90 to about 5 $k_B T$ during the measurement.

This correlates again with previous observations, which indicated that the polymer P_{Phos} has a strong influence on the crystal growth morphology. The simplest picture, which seems to explain this influence at least qualitatively, is based on the idea that different crystal faces exhibit different affinities for the polymer and, thus, lead to different amounts of adsorbed polymers. However, the magnitude and the concentration dependence of the signal shown in Figure 2 are *not* typical for adsorption of the polymers on crystal surfaces and other sources of enthalpy consumption are to be identified.

Polymer Adsorption. To identify the contribution to the exchanged heat arising from polymer adsorption, the crystal dispersion was filtered through a 200 nm pore-size filter, thus removing all larger crystals as confirmed by electron microscopy and dynamic light scattering. The phosphorylated polymer P_{Phos} was then added to the filtered calcite dispersions, resulting in the data shown in Figure 3. Inspection of this figure shows that the signal becomes even *more* endothermic after the large crystals have been removed. The contribution of these large crystals now corresponds to the difference (open circles in Figure 3) between the data for the original calcite dispersion (black squares) and the filtered calcite dispersion (open squares). In this way, the contribution arising from the adsorption of the polymers to the surfaces of the calcite crystals is found to be an entirely *exothermic* process.

The interaction of the added polymers with the large calcite crystals (open circles in Figure 3) is well described by the Langmuir type adsorption model as introduced above. Using eq 6 for the exchanged heat per added polymer, we have two fitting parameters: K and ΔH. The fitting curve in Figure 3 corresponds to the values $K = 31$ mM^{-1} and $\Delta H = -1.77$ J/m^2.

Using the relation $\Delta G_c^0 = -RT \ln K$ for the change in the standard Gibbs free energy change (defined for standard state M^{-1}), we can calculate ΔG_c^0 for the adsorption process of the polymer as -25.6 kJ/mol which corresponds to about 10.3 $k_B T$ per injected polymer. This

quantity is in a physically reasonable range for the following reason. These polymers were optimized and selected on an empirical basis for their function in morphology control, which relies on reversibility and selectivity of polymer adsorption populated by thermal energy.

The value obtained for the equilibrium constant is self-consistent with the assumption of the model, that is, that the concentration of free polymer is much larger than the adsorbed one. As shown in Figures 2 and 3, the polymer concentrations were varied from about 10^{-6} to about 4×10^{-5} M. Inserting these values into eq 1, we obtain that the coverage of the crystal surface changes from a few to about 50%. This is in good agreement with observations by Tsortos and Nancollas[19] who studied the adsorption of polyelectrolytes (at similarly low surface concentrations) onto calcium phosphate crystals.

To estimate the density of polymer adsorbed on the crystal surface, one needs to know the area of an adsorption site, that is, area per polymer, which is out of the scope of this work. Assuming physically reasonable values, however, reveals that indeed the majority of the polymer stays unbound.

The "difference experiments" just described unequivocally show that the adsorption of polymer molecules onto the crystal surfaces is an exothermic process as expected. However, the origin of the strongly endothermic process observed when adding the polymer solution to the filtered calcite dispersion still remains to be clarified. It is compelling to assume that this endothermic process must be related to the interaction of the polymer with a species which is smaller than the lower cutoff of 200 nm as provided by the pore size of the filter. In fact, light scattering measurements on filtered solutions did not disclose the presence of species larger than 20 nm. Furthermore, it seems reasonable to assume that the adsorption of a single polymer onto a calcite crystal involves the same heat of adsorption as long as the crystal is large compared to the length of the polymer, which is about 10 nm.

Interactions between Polymers and Calcium Ions. In addition to the calcite crystals, the calcite dispersion also contains a certain amount of calcium ions, the interaction of which with the polymer molecules might represent another source of enthalpy. To estimate the interactions between the negatively charged polymers and the positively charged calcium ions, the polymer solution was injected into a $CaCl_2$ solution. The concentration of $CaCl_2$ was chosen in such a way that it contained the same Ca^{2+} concentration (7×10^{-5} M) as the previously studied calcite suspension, that is, $[Ca^{2+}] = \sqrt{k_s}$ where k_s is the solubility product of calcite ($k_s = 5 \times 10^{-9}$ M²). The corresponding titration curve is shown in Figure 4. Inspection of this figure shows that the process of adding the P_{Phos} to the $CaCl_2$ solution is endothermic and that the adsorbed heat is larger than for the reference measurement in which the polymer P_{Phos} is injected into pure water.

To exclude potential pH effects and/or influence of another counterion (Cl^-), we prepared also a pure "ionic" $CaCO_3$ solution by strong centrifugation of the calcite solution (at 20 000 rpm for 1 h in a lab centrifuge), which is presumably sufficient to remove all species apart from the dissolved ions in the dispersion. The corresponding titration curve is included in Figure 4. This titration process is again endothermic. The absorbed heat is larger than for titration of the $CaCl_2$ solution but smaller than for the titration of the filtered calcite dispersion. The

(19) Tsortos, A.; Nancollas, G. H. *J. Colloid Interface Sci.* **1999**, *209*, 109.
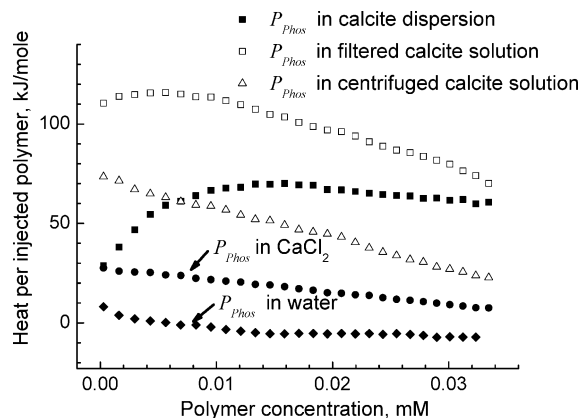
Figure 4. Concentration dependence of the heat per injected polymer P_{Phos} in the calcite dispersion (filled squares, as in Figure 3), in the filtered calcite solution (open squares, as in Figure 3), in the centrifuged calcite solution (open triangles), in a solution of 7×10^{-5} M $CaCl_2$ (filled circles), and in water (diamonds).

difference between the titration curves for the $CaCl_2$ solution and for the ionic $CaCO_3$ solution should primarily reflect (i) the different hydration of the Cl^- and of the CO_3^{2-} (or/and HCO_3^-) ions and (ii) the potential pH effects ($CaCl_2$ in those concentrations is weakly acidic). It would be interesting to disentangle the different contributions and, in this way, study the chaotropic character of the different anions in water, but this is, due to the small difference between these curves, of minor relevance for the present discussion.

The overall endothermic character of the Ca^{2+}/polymer titration curves is somewhat counterintuitive since one might naively expect that the attractive Coulomb interactions between the Ca^{2+} ions and the negatively charged polymers lead to an exothermic signal. However, the endothermic character of this process can be understood in terms of the competition between the polymer/ion, polymer/water, and ion/water interactions: the binding of one Ca^{2+} ion to the polymer distorts the hydration shells of both binding partners and leads to the liberation of many water molecules from these shells. Roughly speaking, the energy gain associated with the binding of the Ca^{2+} ion to the polymer is overcompensated by the energy loss arising from the broken hydrogen bonds. On the contrary, the interaction of the polymer with the crystal is exothermic and therefore of a different nature. One may reason that, for example, this is due to the different hydration of the Ca atoms from the crystal calcite lattice.

Mixture of Polymer Solution and Centrifuged Calcite Dispersion. The difference between the Ca^{2+}/P_{Phos} curves and the previously discussed titration curve obtained by injecting P_{Phos} into the filtered calcite suspension is the last contribution to be discussed. As mentioned above, the concentration of Ca^{2+} ions is the same for both titration processes. However, inspection of Figure 4 (see the signal from the centrifuged suspension) shows that the titration of the filtered calcite suspension gives an endothermic signal which is stronger (by a factor of $^1/_4 - ^1/_5$). This implies that the latter signal must contain additional endothermic contributions, which arise not from the interactions between the phosphorylated polymers and the ions but from an additional solution species. The linear dimension of this additional species should be smaller than $10-20$ nm since we expect the same exothermic adsorption process to occur for all crystals which are large compared to the contour length of the polymer. Thus, we conclude that the calcite dispersion
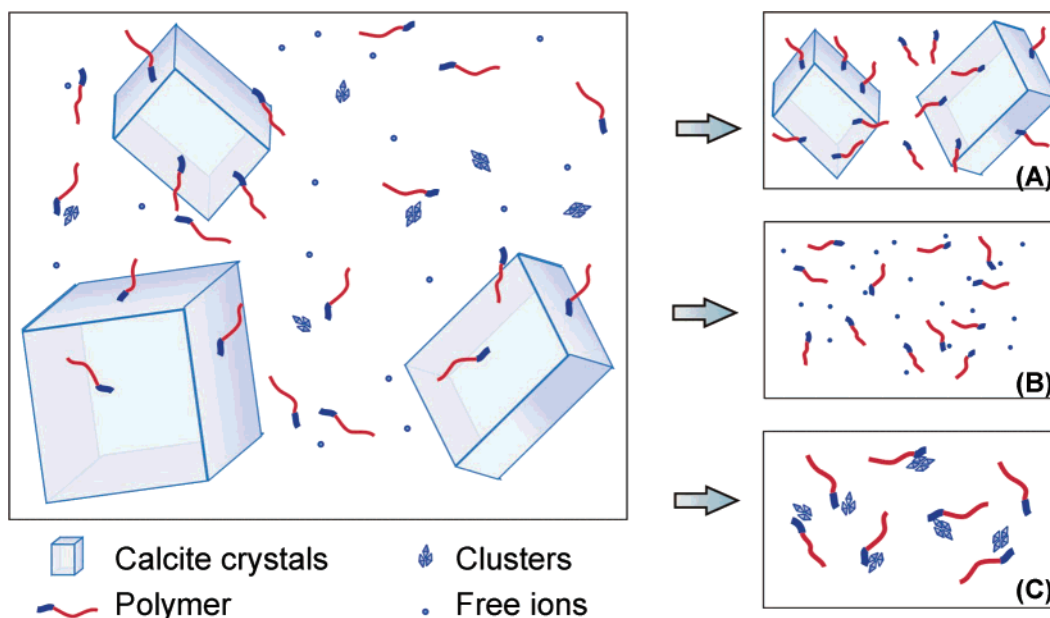
Figure 5. Schematic representation of the P_{Phos} polymers in the calcite dispersion (the relative size of the different species present in the solution is not drawn to scale). The polymer (P_{Phos}) consists of two blocks: a phosphorylated block (blue), which interacts with the crystal surface, and a PEO chain (red). (A) P_{Phos} adsorption on calcite crystals; (B) interaction of P_{Phos} with free ions (as from the measurement with the centrifuged calcite dispersion); (C) P_{Phos} interacting with $(CaCO_3)_p (H_2O)_q$ clusters as postulated in the present article.

contains another solution species of mesoscopic size, presumably very small amorphous calcium carbonate of the type $(CaCO_3)_p (H_2O)_q$ (where $1 < p < 100$). Furthermore, the endothermic character of the interaction may be considered as an indication that by nature this interaction is closer to the one between the polymer and the calcium ions (endothermic), rather than the adsorption of the polymer onto the crystal surface (exothermic). Direct experimental evidence for such a species is still missing. However, it was introduced as an intermediate structure during crystal growth as discussed in ref 20 and could play an important role for scale formation. The role of amorphous nanocluster intermediates in biomimetic mineralization events was recently discussed.[21]

The different contributions to the interaction of P_{Phos} with the calcite dispersion are schematically depicted in Figure 5. Essentially, the heat released from injecting polymer into the calcite dispersion is presented as a superposition of three terms: adsorption of P_{Phos} onto the crystal surfaces (A) and interaction of P_{Phos} with ions (B) and with clusters (C). A quantitative representation is displayed in Figure 6. The three different curves from the injection of polymer into original, filtered, and centrifuged calcite solutions allow us to delimit the relative importance of the three different contributions. Inspection of the two zones attributed to the interactions with ions and with clusters shows that they are of comparable size. This could imply that the concentrations of calcium ions and calcium carbonate in the form of clusters are of the same order of magnitude: $C_{ions} \approx p C_{clusters}$, where C_{ions} is the concentration of free ions and $C_{clusters}$ is the cluster concentration. This low concentration ($C_{clusters} < 5 \times 10^{-5}$ M) would explain why clusters are not detectable with light scattering observation.

Conclusion

We have used ITC measurements in order to study the interactions between doubly hydrophilic block copolymers
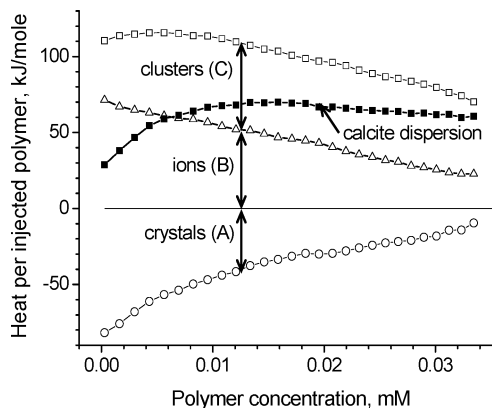
Figure 6. The heat per P_{Phos} polymer injected into the calcite dispersion (filled squares, same data as in Figure 2) is decomposed into three different contributions. (A) The adsorption of P_{Phos} onto calcite crystals as in Figure 5A is an exothermic process (same data as in Figure 3, open circles). (B) The measurement with the centrifuged calcite dispersion (same data as in Figure 4, open triangles) gives the contribution from the interaction of P_{Phos} with free ions as in Figure 5B. (C) The interaction of P_{Phos} with the clusters as schematically shown in Figure 5C is bounded from above by the measurement with the filtered calcite dispersion (same data as in Figure 3, open squares).

and calcite. The most interesting behavior was obtained for block copolymers consisting of a PEO block and a partially phosphorylated butadiene block. The interaction of these block copolymers with sufficiently large calcite crystals can be understood in terms of polymer adsorption, an exothermic process that is well fitted by a Langmuir type adsorption model. Removal of the larger crystals by filtering allows unperturbed observation of a remaining endothermic process characterized by a relatively large absorbed heat, which can only partially be attributed to the interaction of the polymer with Ca^{2+} ions. The additional contribution to this heat is speculatively

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attributed to polymer interaction with a further solution species provided by small clusters or aggregates of calcium carbonate of the type $(CaCO_3)_p (H_2O)_q$ where $1 < p < 100$.

Another interesting result of the present study is the observation that the dilution of the phosphorylated polymer in water is an endothermic process at low polymer concentrations but becomes an exothermic one at larger concentrations. The underlying mechanism, which could be related to the hydration of the polymers and the disruption of water structure (hydrogen bonds), remains to be clarified.