

# Polymer Physics and Superplasticizers

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**Synopsis:** The increased performance of polycarboxylate superplasticizers is generally explained by the steric hindrance they are intended to develop between cement particles. In fact, direct evidence of this is relatively scarce. The only direct measurements to date have been made by atomic force microscopy on model surfaces of magnesium oxide. In this paper, we report very recent measurements using the same technique but on surfaces of calcium silicate hydrate that constitute a more realistic model system. Furthermore, it is shown that the measured interfacial behavior of superplasticizers can be quantified by a scaling law approach borrowed and extended from polymer physics.

**Keywords:** adsorption; atomic force microscopy; scaling laws; steric hindrance; superplasticizers.

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## INTRODUCTION

Polyacrylate superplasticizers, based on comb copolymers with an adsorbing backbone and non-adsorbing side chains, have established themselves as crucial ingredients in concrete for greatly improving workability, strength and durability.<sup>1</sup> Similar polymers have also been reported to be effective with barium titanate,<sup>2</sup> concentrated cemented carbide,<sup>3</sup> magnesia,<sup>3</sup> limestone,<sup>4</sup> and silica.<sup>5</sup>

The linear anionic backbone (typically a polyacrylate or polymethacrylate) of these polycarboxylate esters (PCEs) drives their adsorption onto positively charged cement grains<sup>6,7</sup> and their side non-adsorbing side chains induce steric hindrance between surfaces.<sup>8,9,10</sup> This reduces or suppresses otherwise attractive interparticle van der Waals forces<sup>11,12</sup> or ion correlation forces.<sup>13</sup>

The adsorption behavior of these polymers is therefore an important property for understanding their performance, and defining the relative importance of different molecular structure parameters therein. Atomic force microscopy (AFM), performed with admixtures on magnesium oxide surfaces, suggest that the side chains are coiled rather than stretched.<sup>14,15</sup> This important piece of information demands to be confirmed by measurements in systems closer to cementitious suspensions and with a broader range of variations in molecular structures. Indeed, the measurements on model systems of MgO is not completely inert<sup>16</sup> and a pH of 10 was used, while as cementitious system lay rather around 12.5.

In this paper, we present a summary of a larger experimental investigation using calcium silicate hydrate surfaces in AFM experiments.<sup>17</sup> Those experiments built upon expertise for using atomic force microscopy as a colloidal probe in such systems, but were conducted in the absence of superplasticizers.<sup>18,19</sup> We show how numerous conformational characteristic of these polymers can not only obtained by this method, but also predicted from a model derived from a scaling approach. With respect to the original paper, we present the main results in a more synthetic way in order to relate them more directly to their impact on superplasticizer behavior.

## THEORY

### General statements and polymer description

In polymer physics the conformation of polymers is often successfully described by scaling laws. The strength of such relations is based on the dependence of a given property (ex: radius of gyration) on molecular parameters (ex: chain length). This means for example that the radius of gyration of a linear chain,  $R_g$ , is predicted to vary with  $3/5$  power of the chain length, which has been confirmed experimentally in good solvents. The expression takes the form:

$$R_g = aP^{3/5} \quad (1)$$

where  $P$  is the number of units in the chain and  $a$  is a numerical prefactor, linked to be not necessarily equal to the monomer dimension.

It should be noted that the numerical prefactors (in the above case  $a$ ) are by definition inaccurate. In our example, this means that the absolute value of a chain length is not accurate. However, the relative change in radius of gyration from a change in chain length is correctly captured, which is the real power of the scaling approach. In the expressions below, great care has been taken to attempt to obtain numerical prefactors that are in quite close agreement with experimental data.<sup>17</sup> However, these factors maintain an inaccuracy that is inherent to the scaling law approach they were derived from. It should also be noted that the form of presenting the data chosen here demonstrates in a more direct way the quality of the model. The original paper on the other hand proposed a more detailed discussion on the quality of the fit, which is beyond the scope of the present paper.

Recently, a scaling law approach was proposed for comb homopolymers in solution.<sup>20</sup> This work has been extended to capture the behavior of comb copolymers both in solution and on adsorbed interfaces.<sup>17</sup> This paper presents the main results of that work without repeating the detailed derivation that can be found in the original work.

Following the notation as introduced by Gay and Raphael,<sup>20</sup> we described the structure our comb homo-polymers as follows. The polymer backbone is defined as the assemblage of  $n$  repeating structural units, each containing  $N$  monomers and one side chain of  $P$  monomers. The polymers under consideration behave as a flexible backbone worm (FBW) as defined by the same authors.<sup>20</sup>

### Solution conformation

In the FBW conformation, polymers in solution are described as a flexible chain of

cores (Fig. 1) each containing  $n_c$  side chains and having an end-to-end distance of  $R_c$  respectively given:

$$n_c^2 = \frac{P}{N} \left( \frac{a_p}{a_N} \right)^2 \quad (2)$$

and

$$R_c = \left( \frac{a_p (1-2\chi)}{a_N} \right)^{1/5} a_p P^{7/10} N^{-1/10} \quad (3)$$

where  $a_N$  and  $a_p$  are respectively the monomer sizes for the backbone and the side chains and  $\chi$  is the Flory parameter.

The polymer radius of gyration of the polymer is then:

$$R = \left( \left( \frac{a_N}{a_p} \right)^2 \frac{(1-2\chi)}{2} \right)^{1/5} a_p P^{2/5} N^{1/5} n^{3/5} \quad (4)$$

For the polymers described here,  $a_p = 0.25$  nm (methacrylate),  $a_N = 0.36$  nm (ethylene oxide) and  $\chi = 0.37$ .<sup>21,17</sup>

In the adsorbed state, the polymer chain seems best described by a flexible chain of hemispheres, each containing  $n_{AC}$  side chain, with a radius of  $R_{AC}$  given by:

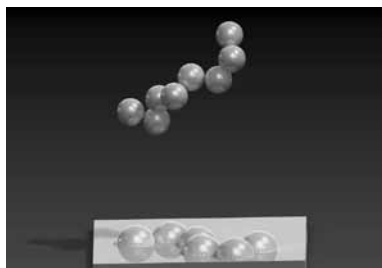


Fig. 1—Schematic representation of a comb copolymer in solution (chain of spherical cores, each of radius  $R_c$ ) and one adsorbed on a mineral surface (chain of hemispheres, each of radius  $R_{AC}$ ). Reproduced from Reference 17.

$$n_{AC} = \frac{a_p}{a_N} \left( 2 \frac{P}{N} \right)^{1/2} \quad (5)$$

and

$$R_{AC} = \left( 2\sqrt{2}(1-2\chi) \frac{a_p}{a_N} \right)^{1/5} a_p P^{7/10} N^{-1/10} \quad (6)$$

In addition the surface occupied by each molecule is:

$$S = \frac{\pi}{\sqrt{2}} a_N a_p \left( 2\sqrt{2}(1-2\chi) \frac{a_p}{a_N} \right)^{2/5} P^{9/10} N^{3/10} n \quad (7)$$

Schematic illustration of how the solution and adsorbed conformations may be thought about is illustrated in Fig. 1.

## Steric hindrance

When two surfaces on which polymers are adsorbed in the above conformation approach, a steric force develops when the adsorbed layers start to overlap. This happens when the surface to surface distance,  $D$ , is equal to  $2 R_{AC}$  as illustrated in Fig. 2.

Assuming the tip of the AFM is hemispherical with a radius  $R_{tip}$ , the steric force can be calculated to be:

$$F = \beta \left( \frac{5}{2^{1/3}} R_{AC}^{2/3} - \frac{1}{2} D^{-1/3} \left( 3D + 4 \cdot 2^{2/3} R_{AC} \left( \frac{R_{AC}}{D} \right)^{2/3} \right) \right) \quad (8)$$

with

$$\beta = \frac{2\pi k_B T R_{tip}}{\alpha} P^{-29/30} N^{-13/30} \quad (9)$$

and:

$$\alpha = \pi \cdot 2^{-3/10} a_P^{5/3} a_N \left( (1 - 2\chi) \frac{a_P}{a_N} \right)^{2/15} \quad (10)$$

## MATERIALS AND METHODS

Polymers were produced by radical co-polymerization and were purified by ultra filtration with membranes having size exclusions of 1 to 10 kD, depending on the size of the side chains. Details information on the polymers is provided elsewhere.<sup>17</sup>

For the AFM experiments, solutions of these polymers were prepared by dissolution in a 5 mM calcium hydroxide solution to obtain 10 polymer solutions at 10 mg/L. This polymer dosage was found sufficient to fully cover the surface, so that concentration effects on the surface could be neglected. Results therefore all pertain to situations of initial full surface coverage.

All experiments were performed in a CO<sub>2</sub> free glove box in order to prevent carbonation of hydroxide solutions. Inside, a commercial atomic force microscope (Nanoscope IIIa Quadrex, Veeco Inst., Santa Barbara, CA) was used. For all studies in calcium hydroxide solutions, an adapted commercial fluid cell was used. The temperature of the surrounding wall was maintained at 25°C (77°F) and humidity controlled in order to avoid evaporation of the solution. For topographical investigations of C-S-H and polymer surfaces, oscillating contact mode AFM (Tapping-AFM) and silicon nitride probes with a nominal spring constant of 0.03 N/m have been used. Force measurements were carried out on flat C-S-H surfaces with silicon nitride DNP-S microlever of spring constant varying between 60 mN/m and 600 mN/m, Veeco Inst.) covered with C-S-H following a protocol described elsewhere.<sup>22</sup> All experiments started with a characterisation of the surface in absence of polymer and then in presence of polymer.<sup>17</sup> A schematic illustration of an AFM is shown in Figure 3, while Figure 4 shows an example of an image obtained in absence and in presence of a superplasticizer.

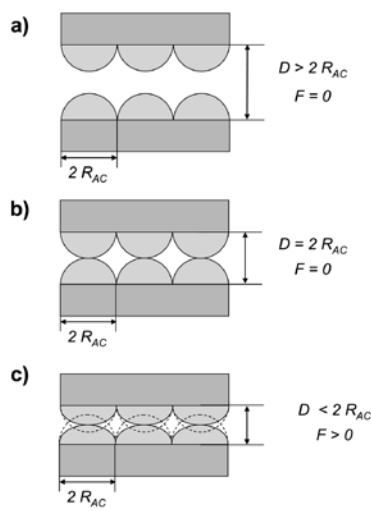


Fig. 2—Schematic illustration of the approach of layers illustrating the the steric hindrance force begins once the adsorbed layers begin to overlap (adapted from Reference 17).

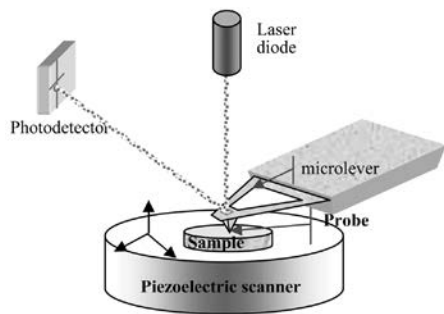


Fig. 3—Schematic of the multimode atomic force microscope.

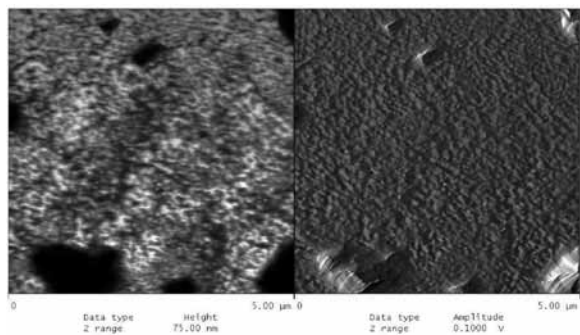


Fig. 4—Typical AFM image (5x5 μm) of C-S-H surface covered by a polymer layer observed in 5 mM Ca(OH)<sub>2</sub> solution.

## RESULTS AND DISCUSSION

### Polymer conformation

Results of polymer conformation in solution agree rather well with Equation (4)<sup>17</sup> and have also been confirmed recently by neutron scattering measurements.<sup>23</sup> Concerning the adsorbed conformation, the first property examined is the surface occupied by a polymer at the adsorption plateau (no more polymer can be adsorbed). Experimental values can be obtained from the measurements of Perche performed on MgO model systems.<sup>24</sup> We find that Equation (7) shows a very good correlation with the experimental values as shown in Figure 5.

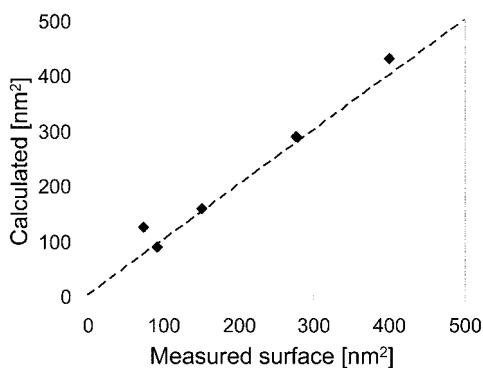


Fig. 5—Comparison between the surfaces occupied by a polymer for experimental values and ones calculated with Equation (7). The discontinuous line shows the one to one relation.

Another important aspect of polymer conformation in the adsorbed state is the layer thickness. This can be obtained from AFM force measurements identifying the point at which the force begins to rise above zero. The corresponding separation distance is expected to be twice the value layer thickness. Determining layer thickness from such measurements has shown a very good correlation with values of  $R_{AC}$  from Equation (6).<sup>17</sup> Here we choose a more practical representation of the data to illustrate this good correlation (Fig. 6).

### Steric force

An example of two force measurements is shown in Figure 7.<sup>17</sup> On each graph the crosses show five repetitions and the continuous line shows the fitted curve. The illustrations shown for two polymers with very different side chain lengths indicate that Equation (7) well captures the dependence of separation distance and layer thickness on the magnitude of the steric force. It is important here to recall that the experiments are done with polymer dosages that insure full surface coverage. This means that the differences between S3 and S10 in Figure 6 do not come from adsorption differences but truly from conformational differences.

In the data analysis procedure for Figure 7, the values of  $\beta$  were however fitted. The next step of the analysis therefore consists of examining whether the dependence of

this parameter on polymer structure is well captured by Equation (9). Once again we find a good agreement as shown in Figure 8. This last step involves an estimation of the tip radius. The value used in Equation (9) is 15 nm, however, taking into account

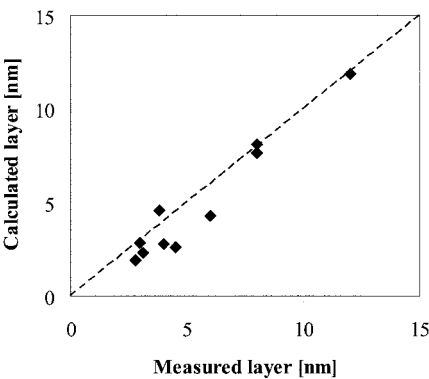


Fig. 6—Comparison between measured and calculated prefactor from Equation (8). The discontinuous line shows the one to one relation.

inaccuracies in the various steps of the derivation, this would really correspond to about 45-50 nm. Considering errors in the other estimation of the tip radius this is a reasonable value.<sup>17</sup>

All these results point clearly to the fact that side chains are coiled and not stretched as often represented (mainly for schematical purposes). They also demonstrate in a convincing way the layer thickness lies within a few number of nanometers and not in tens or hundreds of nanometers as had been reported in the past.<sup>11</sup> It is therefore quite probable that those measurements were biased by an artefact due to the mineral reactivity.<sup>25</sup>

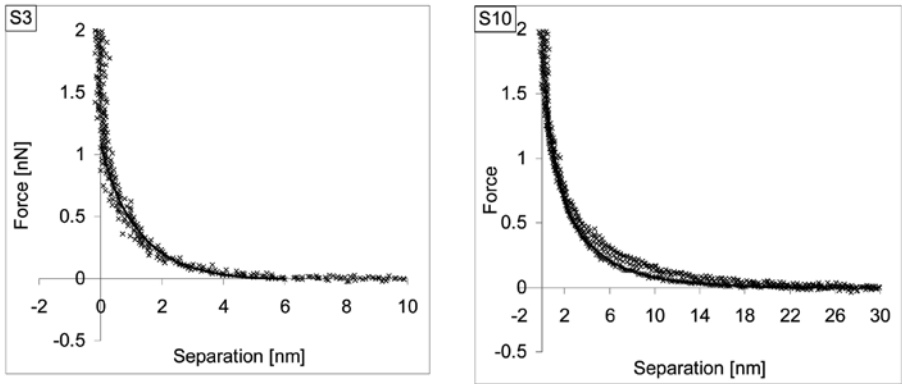


Fig. 7—Force distance curves. The dots show data from five different runs. The continuous lines show fit obtained with Equation (8). S3 has side chains of 1,000 g/mol and S10 of 10,000 g/mol). Adapted from Reference 17.



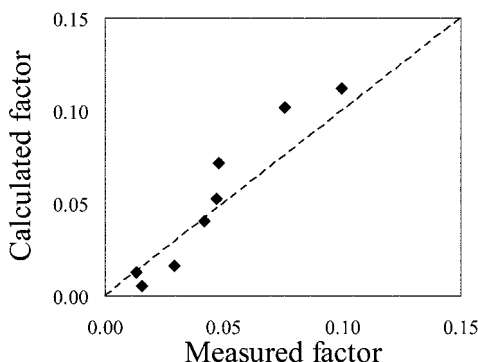


Fig. 8—Comparison between the measured and calculated prefactor  $b$ , using Equation (9). The value of  $R_{tip}$  is taken to be 15 nm.<sup>17</sup>

## CONCLUSIONS

A scaling law approach has been presented which captures the conformation behavior of superplasticizers both in solution and on the adsorbed state. Data from the literature has provided a check on the radius of gyration in solution and the surface occupied by each polymer at the saturation plateau. This has been completed by atomic force measurements that have confirmed that the model correctly captures the molecular structure effect on the polymer layer thickness and the resulting effect on steric hindrance. This represents an important step in understanding the quantitative behavior of superplasticizers.

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