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# Comb-Shaped Polymers as Nanostructure Modifiers of Calcium Silicate Hydrate: A $^{29}\text{Si}$ Solid-State NMR Investigation

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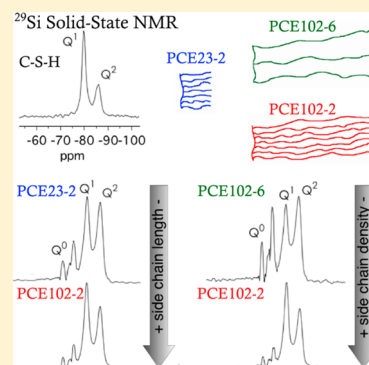
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## S Supporting Information

**ABSTRACT:** Calcium silicate hydrate gel (C–S–H) is the complex phase mostly responsible for the binding properties and the mechanical resistance of Portland cement. The clarification of the C–S–H nanostructure and how the presence of organic additives affects it is still an intriguing and not trivial task, especially due to C–S–H scarce crystallinity and intrinsic complexity. In this work, we exploited  $^{29}\text{Si}$  solid-state nuclear magnetic resonance (NMR) to investigate the effects of different comb-shaped superplasticizers on the silicate structure. The analysis of  $^{29}\text{Si}$  solid-state NMR spectra shows that the additives increase the degree of polymerization and hence the average length of the silicate chains in C–S–H. This finding correlates well with the increase of the globule dimensions estimated by means of small angle scattering techniques showing that the comb-shaped polymers are able to tune the overall dimension of the C–S–H globule. This effect is dependent on the molecular architecture of the superplasticizer and allows a molecular imprinting to the globular structure of the C–S–H gel.



## INTRODUCTION

The hydrated phase mostly responsible for the binding properties and for the final mechanical resistance of Portland cement is calcium silicate hydrate (shortly, C–S–H). This colloidal phase<sup>1</sup> is formed as a consequence of the hydration of tricalcium and dicalcium silicate, through complex dissolution and reprecipitation processes. Its structural properties have been studied since long time by means of both experimental and theoretical approaches, in the attempt to provide a clear picture of this material. Anyway, because of the intrinsic complexity of the system being mainly amorphous, this effort has been only partially fulfilled.

In the last decades solid-state nuclear magnetic resonance (SS-NMR) spectroscopy has been widely used in the studies of cement-based materials.<sup>2–4</sup> High-resolution magic angle spinning (MAS) SS-NMR can investigate the local electronic structure, providing detailed structural information on the chemical environments of the nuclei. This is particularly useful in the investigations of cement pastes since  $^{29}\text{Si}$  isotropic chemical shifts reflect the structural surroundings of a silicon atom, and they can be associated to the different types of  $\text{SiO}_4$  tetrahedra, whose relative amounts can also be determined.<sup>5–8</sup> The different  $Q^n$  sites, where  $Q$  represents the  $\text{SiO}_4$  tetrahedron and  $n$  refers to the number of Si–O–Si bonds, have different  $^{29}\text{Si}$  isotropic chemical shifts in solid silicates.<sup>9–11</sup> Previous  $^{29}\text{Si}$  MAS NMR studies suggested that C–S–H has a disordered layered structure made of dreierketten linear silicate chains

similar to that of tobermorite (Figure 1), the  $^{29}\text{Si}$  MAS NMR spectrum being characterized by the presence of end-group  $Q^1$  and middle-group  $Q^2$  resonances.<sup>12,13</sup>

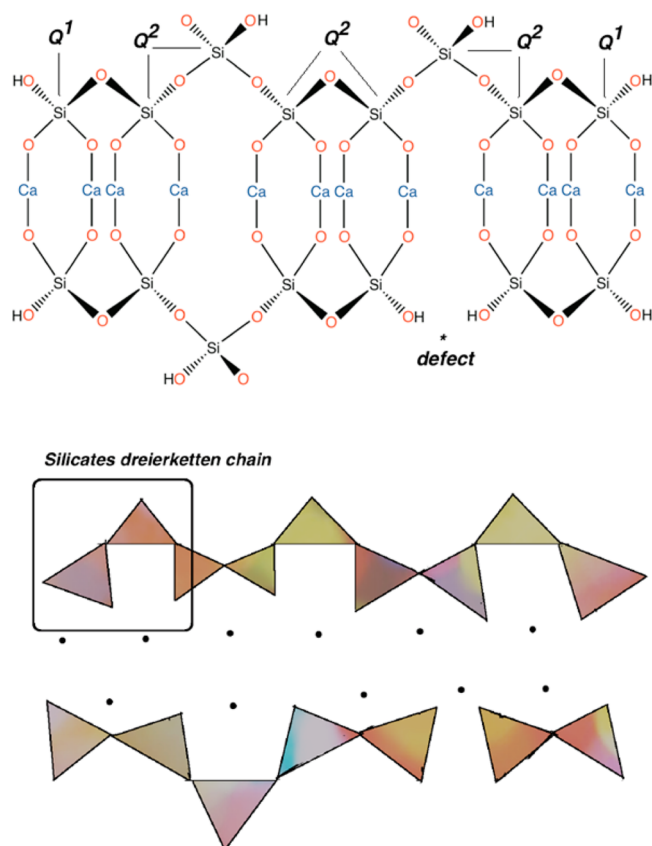
Nowadays, almost all the cement formulations contain organic polymers, whose role is to confer specific characteristics to the paste. In particular, superplasticizers are essential components of every formulation, as they confer high workability to the pastes keeping low the water content. Last generation superplasticizers are comb-like polymers, made of polycarboxylic chains partially esterified with polyethylene oxide lateral chains. One of the most interesting issues in the cement research is the assessment of the effect of these organic polymers on the C–S–H nanostructure. Indeed, understanding the organic/inorganic interactions on a molecular level could enable tailoring the bulk properties by controlling the nanoscale structure, through a bottom-up process. Although SS-NMR has been extensively applied for studying organic–inorganic composite materials,<sup>14,15</sup> only a limited number of papers reported on this topic,<sup>8,16–24</sup> showing that  $^{29}\text{Si}$  SS-NMR can be successfully exploited to investigate the effects of polymers on the silicate network. In particular, the relative intensities of  $Q^2$  and  $Q^1$  signals are an indicator of the silicate polymerization degree, which can change in the presence of additives.

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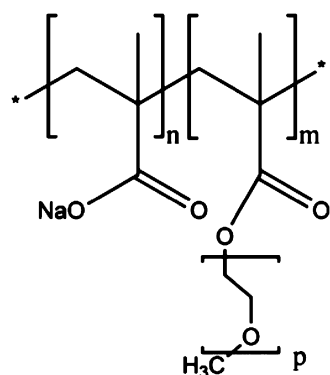


**Figure 1.** Two schematic representations of the tobermorite structure. (top)  $Q^n$  sites are explicitly highlighted (bottom). Triangles represent silicate tetrahedrons arranged in the well-known silicate dreierketten chains. The calcium atoms (circles) are located at the center of Ca–O octahedra.

This article aims to investigate the effect of comb-shaped superplasticizers on the nanostructure of C–S–H through  $^{29}\text{Si}$  SS-NMR measurements. Infrared spectroscopy has been used to further inspect the organic/inorganic interactions.

## EXPERIMENTAL SECTION

The chemically pure batch of synthetic  $\text{C}_3\text{S}$  (CTG-Italcementi, Bergamo) had a specific surface area of  $0.65 \text{ m}^2/\text{g}$  (BET). Polycarboxylic esters (PCEs) were obtained from BASF. They are polymethacrylic chains partially esterified with polyethylene oxide lateral chains. The molecular structure is sketched in Figure 2. Each polymer is identified by the acronym  $\text{PCE}p-n$ ,



**Figure 2.** Sketch of the PCEs molecular formula.

where  $p$  is the number of repeating PEO units in the lateral chains and  $n$  identifies the number of free carboxylic groups per esterified group.

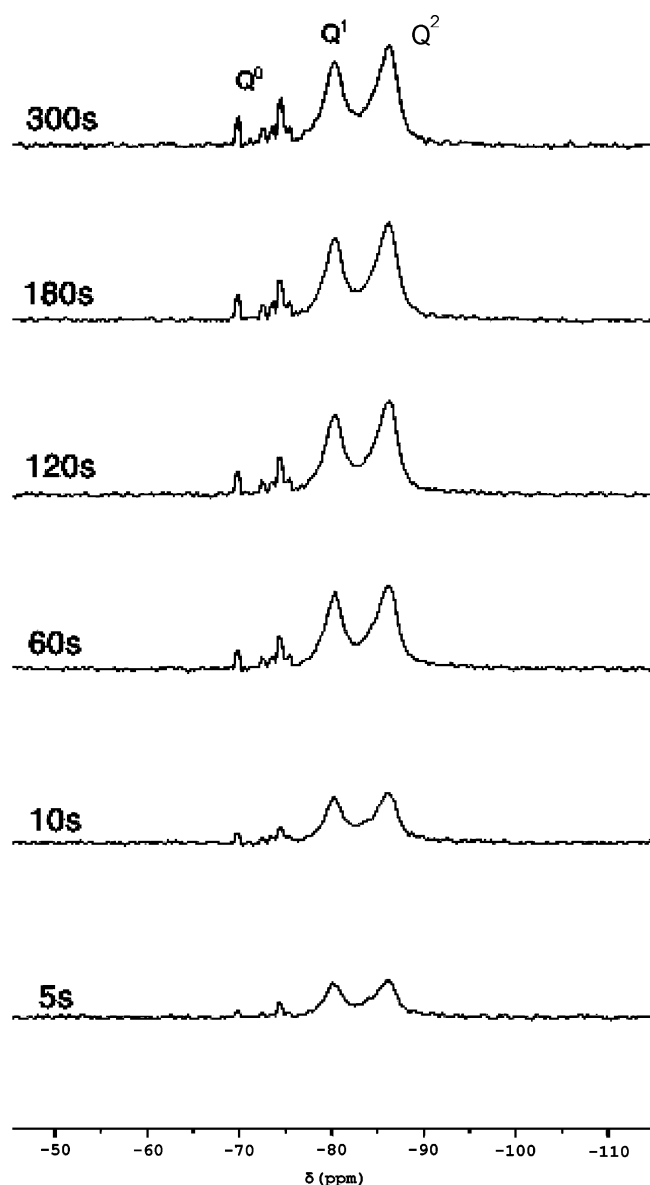
Shortly resuming the PCE characteristics: PCE23–2 and PCE23–6 have PEO side chains, which are five times shorter than PCE102–2 and PCE102–6, while PCE23–6 and PCE102–6 have more free carboxylic groups on the backbone. Previous studies<sup>25,26</sup> have shown that the adsorption of PCEs on cementitious phases is higher for molecules with shorter side chains and a lower side chain density.

Synthetic C–S–H was prepared by hydrating 4 g of pure tricalcium silicate ( $\text{C}_3\text{S}$ ) in 1150 g of pure water or of polymer solution. Two sets of modified C–S–H were synthesized, respectively, with low concentration and high concentration of PCE. The low concentration set (L series) contained 0.4 g of polymer per 100 g of dry  $\text{C}_3\text{S}$ ; the high concentration set (H series) was obtained hydrating the powder with 40 g of polymer per 100 g of dry  $\text{C}_3\text{S}$ . The water and the solutions were degassed to avoid carbonation. The hydration reaction was conducted at  $25^\circ\text{C}$  for 40 days in sealed polyethylene bottles. The dispersions were filtered, and the final water content was standardized by dehydrating the samples at  $60^\circ\text{C}$  in a  $\text{N}_2$  atmosphere. This synthetic route is known to minimize the  $\text{Ca}(\text{OH})_2$  content while forming quite polydisperse C–S–H phase, which is usually referred to as C–S–H (I).<sup>27</sup> Further specific details on the synthesis can be found elsewhere.<sup>28,29</sup> Table 1 summarizes the characteristics of the polymers and of the pastes synthesized for the investigation.

**Table 1. Characteristics of the Polycarboxylate Superplasticizers and Concentration of Polymers in the Pastes**

sample acronym	number of monomeric units of PCE side chain ( $p$ )	density of PCE side chains ( $n:m$ )	PCE concentration in water ( $\text{mg/mL}$ )
C–S–H			
L_PCE102–2	102	2:1	$1.4 \times 10^{-2}$
L_PCE102–6	102	6:1	$1.4 \times 10^{-2}$
L_PCE23–2	23	2:1	$1.4 \times 10^{-2}$
L_PCE23–6	23	6:1	$1.4 \times 10^{-2}$
H_PCE102–2	102	2:1	1.4
H_PCE102–6	102	6:1	1.4
H_PCE23–2	23	2:1	1.4
H_PCE23–6	23	6:1	1.4

The  $^{29}\text{Si}$  NMR spectra were collected on a dual channel Varian Infinity Plus 400 spectrometer operating at Larmor frequencies of 400.03 and 79.44 MHz for  $^1\text{H}$  and  $^{29}\text{Si}$  nuclei, respectively, using a 7.5 mm CP-MAS probe-head. All the experiments were performed at room temperature, using air as spinning gas. Spectra were obtained using a Direct Excitation (DE) pulse sequence with high power proton decoupling and a MAS frequency of 4 kHz, accumulating 660 transients. Spectra were recorded with different recycle delays (from 5 to 300 s, see Figure 3) to find suitable conditions to obtain quantitative spectra. A recycle delay of 300 s is necessary to achieve a complete relaxation. This value is much larger than that commonly used to obtain quantitative  $^{29}\text{Si}$  NMR spectra of cements, possibly due to the fact that the formulations here investigated do not contain  $\text{Fe}^{3+}$  ions, able to reduce the longitudinal relaxation time ( $T_1$ ) of  $^{29}\text{Si}$ . However, in order to reduce the experimental times, all the spectra were recorded

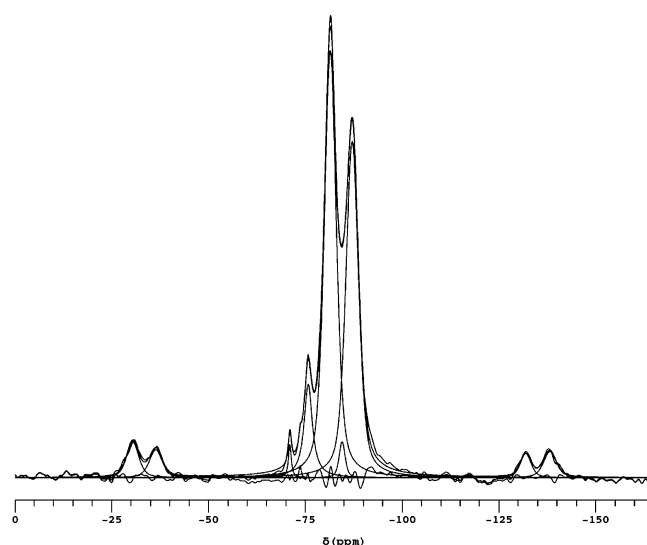


**Figure 3.**  $^{29}\text{Si}$  DE-MAS NMR spectra obtained with the recycle delays indicated.

with a recycle delay of 60 s, and the peak areas, obtained through spectral fittings and also taking into account spinning sidebands (Figure 4), were rescaled to the quantitative areas through suitable scaling factors. These were calculated as the ratios between the areas of the peaks at the two different pulse delays determined for one sample, under the reasonable assumption that the  $^{29}\text{Si}$   $T_1$  relaxation times were the same for all the cement pastes.

Infrared spectra were acquired in the range 4000–400  $\text{cm}^{-1}$ , with a Nexus 870-FTIR (Thermo-Nicolet), using a 4  $\text{cm}^{-1}$  resolution and 64 scans, with a DTGS-TEC detector. To register the spectra, the samples were mixed with KBr with a sample/KBr weight ratio of  $\sim 1/100$  and compressed to obtain pellets.

The effective amount of polymer in each sample has been determined by thermal gravimetric analysis (see Supporting Information, Figure SII). In particular, the mass losses (in the range 200–500  $^{\circ}\text{C}$ ) due to the presence of adsorbed polymers are about 7.0% (and 0.4%) for PCE102–6, 7.5% (and 0.4%) for



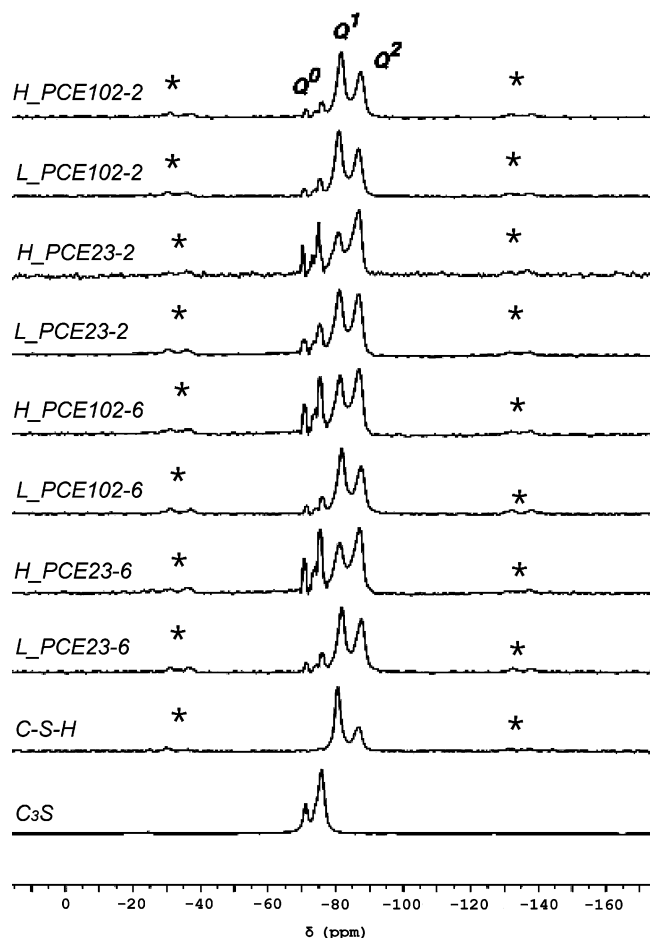
**Figure 4.** Example of fitting of  $^{29}\text{Si}$  DE-MAS NMR spectrum.

PCE23–6, 7.8% (and 0.2%) for PCE102–2, and 9.4% (and 0.2%) for PCE23–2 in the case of the H (and L) series, respectively. The errors in the determination were about 0.9% in the case of H series and 0.1% for the L series. These results show that C–S–H formed in the presence of low amounts of PCE almost completely incorporates the polymer, while in the samples prepared with high concentration of PCE, it only retains a portion of the available polymer approximately ranging from 15 to 25%.

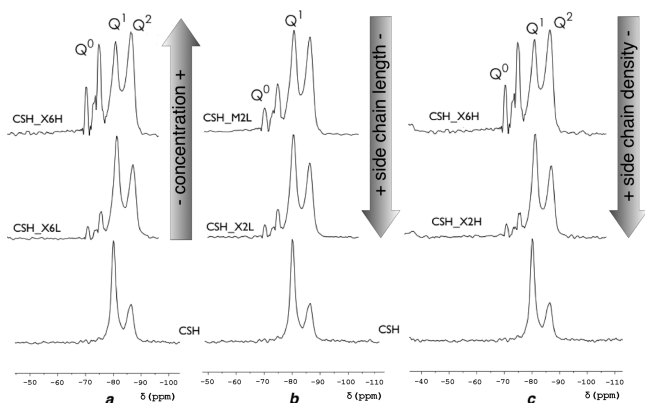
## RESULTS AND DISCUSSION

The  $^{29}\text{Si}$  DE-MAS NMR spectra of all samples are shown in Figure 5. The spectrum of  $\text{C}_3\text{S}$  presents typical  $\text{Q}^0$  signals ( $-70/-76$  ppm) attributed in the literature to the monoclinic form.<sup>10,30</sup> These resonances disappear with the hydration: the spectrum of pure C–S–H is characterized by the presence of very intense  $\text{Q}^2$  and  $\text{Q}^1$  signals only ( $-80/-86$  ppm), in agreement with the literature.<sup>11,13</sup> The presence of very weak  $\text{Q}^0$  signals indicates that  $\text{C}_3\text{S}$  has almost completely reacted. However,  $\text{Q}^0$  signals are clearly observed in the spectra of modified C–S–Hs, indicating that part of  $\text{C}_3\text{S}$  remains unreacted in the presence of the organic additives.

The set of samples investigated allowed the modifications of the silicate structure to be studied at different (i) concentrations of additive, (ii) side chain lengths of the additive, and (iii) side chain densities of the additive. A selection of representative  $^{29}\text{Si}$  DE-MAS spectra showing the effects of these three variables is reported in Figure 6. The experimental and data analysis procedures described in the Experimental section allowed quantitative peak areas (in the following indicated as  $Q^i$  for the sake of simplicity) to be extracted from  $^{29}\text{Si}$  spectra and used to calculate useful structural parameters, such as the degree of silicate polymerization, DP, ( $Q^2/Q^1$ ) and the reactivity  $100(Q^1 + Q^2)/(Q^0 + Q^1 + Q^2)$ . Moreover, it is straightforward to show that in the case of missing  $\text{Q}^3$  signals the mean silicate chain length (MCL) can be easily calculated from DP as it is given by  $2(\text{DP} + 1)$ .<sup>8</sup> The values obtained for these three parameters for each sample are reported in Table 2 and Figure 7. DP increases in the presence of the organic additives from 0.61 (C–S–H) to 1.55 (H\_PCE23–6). This means that C–S–H is characterized by very short silicate chains that become longer in the presence of the additives. In



**Figure 5.**  $^{29}\text{Si}$  DE-MAS NMR spectra of  $\text{C}_3\text{S}$  (bottom) and C-S-H samples, acquired at a MAS frequency of 4 kHz and a recycle delay of 60 s. Spinning sidebands are marked with asterisks.



**Figure 6.**  $^{29}\text{Si}$  DE-MAS spectra of some representative samples. The effects of (a) concentration; (b) side chain length; and (c) side chain density can be clearly observed.

$\text{H\_PCE23-6}$ , where DP assumes its highest value, silicate chains are formed on average by three  $\text{Q}^2$  and two  $\text{Q}^1$ . DP increases by increasing the concentration of additive, as a result of the higher amount of adsorbed polymer. Regarding the effects of the chemical structure of the polycarboxylate, it is possible to observe that shorter side chains favor the silicate polymerization ("PCE23" series samples always show higher DP values than the corresponding samples of "PCE102" series).

The side chain density of the polymer also affects DP. In the case of the longest side chains ("PCE102" series), at low concentration, the effect of this parameter is negligible, while at high concentration DP is higher when the density is lower (i.e., in the sample  $\text{H\_PCE102-6}$ ). The two polymers belonging to the "PCE23" series show similar DP values when mixed with  $\text{C}_3\text{S}$  at high concentration. At low concentration, the  $\text{L\_PCE23-2}$  sample presents a higher DP value than  $\text{L\_PCE23-6}$ .

In all cases, the presence of the organic polymers decreases the reactivity of  $\text{C}_3\text{S}$ . The drop in the reactivity is higher increasing the concentration of additive. The "PCE23 series" is slightly more effective than "PCE102 series" in reducing the reactivity: this is consistent with the higher retarding power of  $\text{PCE23-2}$  and  $\text{PCE23-6}$  with respect to  $\text{PCE102-2}$  and  $\text{PCE102-6}$ .<sup>31</sup> The influence of side chain density is very small.

In previous papers it has been reported that FTIR in the near-infrared region can be used both to investigate the reaction of a hydrating cement pastes<sup>32</sup> and the state of water inside the pores of the developing C-S-H gel.<sup>33</sup> Moreover, some bands in the mid-infrared region of the FTIR spectrum are indicative of the polymerization degree of calcium silicate hydrate.<sup>34</sup> Figure 8 shows the FTIR spectra registered on all the samples. The band centered at  $813\text{ cm}^{-1}$  can be assigned to the Si-O stretching of  $\text{Q}^1$  tetrahedra: this band is reported to increase in intensity with increasing C/S ratio, i.e., with low polymerized samples. In our case, this band is well-defined in the C-S-H sample, while it appears less prominent in the samples containing PCEs. Additionally, the band at  $660\text{ cm}^{-1}$ , due to Si-O-Si bending, is reported to have low intensity and large width in poorly polymerized phases. This is the case for the pure C-S-H samples, while the above-mentioned band is more defined in C-S-H/PCE samples (see Figure 8). All these findings strengthen the evidence provided by SS-NMR that the organic additives increase the polymerization of the silicate in the C-S-H nanostructures.

In a previous paper<sup>29</sup> some of the authors of the present study have investigated the very same gels synthesized with 0.4% of PCE (L series) by a SAXS/SANS combined experiment highlighting the effect of the polymer on the C-S-H base unit. The model applied to analyze the small angle curves<sup>28</sup> was based on the Colloidal Model-II by Jennings,<sup>35</sup> that describe the C-S-H gel as a hierarchical system, where the arrangement of disk-like units of C-S-H (sometimes referred to as globules or "bricks") generates a superstructure being mass-fractal in nature.<sup>36</sup> The main outcome from the SANS/SAXS analysis is the estimation of the equivalent dimension of the globule as a function of the added polymer. Since the MCL refers to the average number of tetrahedral  $\text{SiO}_4$  units constituting a single silicate chain, it is possible to convert this value to a real dimension by multiplying it by the length of the edge of the tetrahedron. Using geometrical relations, this value can be estimated to be about  $2.6\text{ Å}$  if the Si-O bond length is around  $1.6\text{ Å}$ . This is also in agreement with the literature on C-S-H phases<sup>37</sup> where the distance between the Si and the second shell of O is about  $4.2\text{ Å}$ , and hence, the tetrahedron edge is  $4.2 - 1.6 = 2.6\text{ Å}$ . Following the above-mentioned conversion, the chain length estimated for the entire series of investigated samples is reported in Table 2 along with the equivalent dimension of the basic unit (globule equivalent diameter). The comparison between these two quantities shows that there is a strong correlation between the MCL and the average dimension of the globule (see Figure 9), where, as the



Table 2. Degree of Polymerization (DP), Reactivity, and Mean Silicate Chain Length (MCL) of the Different Samples<sup>a</sup>

sample	DP( $Q^2/Q^1$ )	reactivity ( $100(Q^2 + Q^1)/(Q^0 + Q^1 + Q^2)$ )	MCL ( $((Q^2/Q^1) + 1) \times 2$ )	estimated chain length (Å)	globule diameter (nm) <sup>29</sup>
C–S–H	0.61	94	3.22	8.4	6.2
L_PCE23–6	0.96	86	3.92	10.2	7.3
H_PCE23–6	1.55	69	5.10	13.3	
L_PCE102–6	0.89	87	3.78	9.8	7.9
H_PCE102–6	1.33	72	4.66	12.1	
L_PCE23–2	1.25	81	4.50	11.7	12.4
H_PCE23–2	1.42	72	4.84	12.6	
L_PCE102–2	0.80	87	3.60	9.4	6.4
H_PCE102–2	1.08	77	4.16	10.8	

<sup>a</sup>The values were obtained from the fitting of <sup>29</sup>Si DE-MAS NMR spectra. The uncertainties on the values of the degree of polymerization, reactivity and mean silicate chain length are  $\pm 0.04$ ,  $\pm 3$ , and  $\pm 0.08$ , respectively. Estimated chain lengths are calculated as  $MCL \cdot 2.6$  Å, as described later in the text. The C–S–H globule equivalent diameters obtained by a SANS/SAXS investigation<sup>29</sup> are also reported.

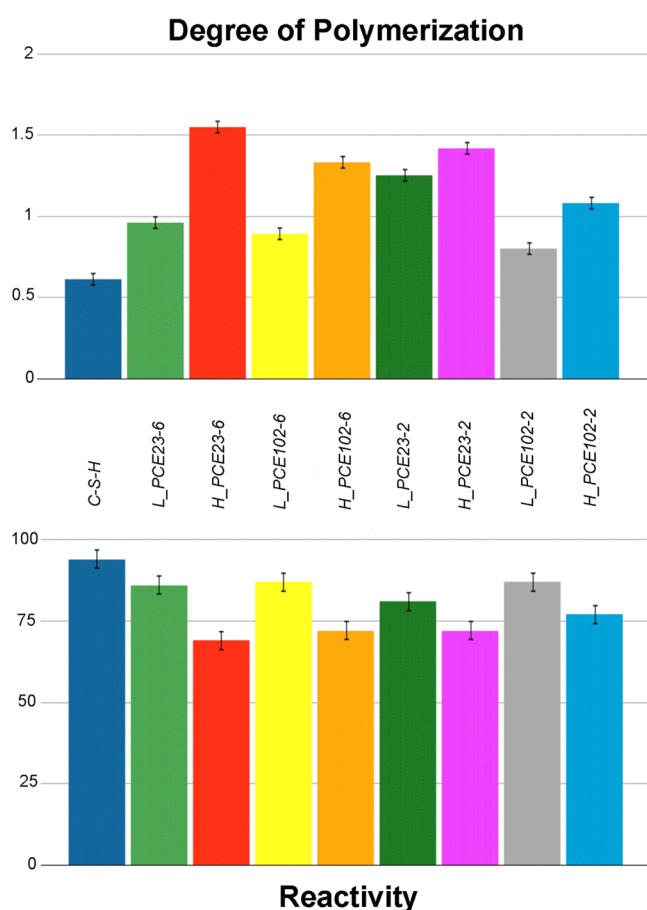


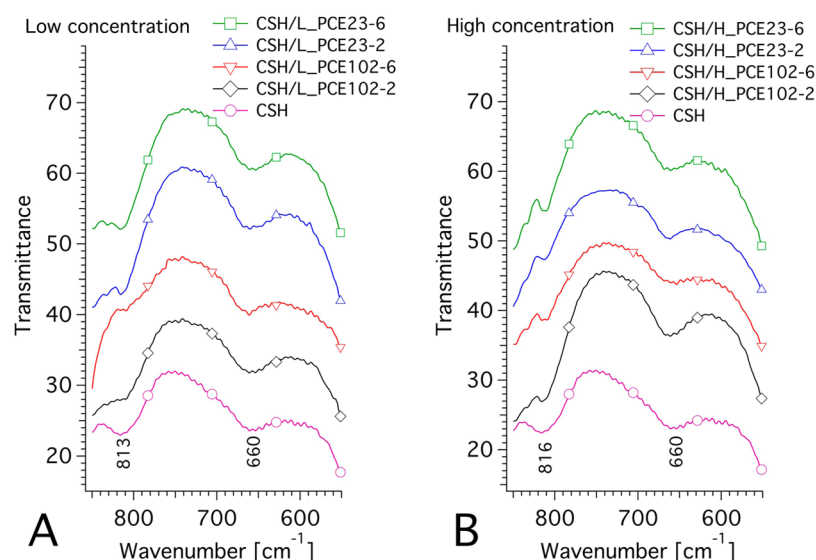
Figure 7. Degree of polymerization (above) and reactivity (below) of the different samples. The values were obtained from the fitting of <sup>29</sup>Si DE-MAS NMR spectra.

silicate chain increases in length, also the globule size becomes greater. In particular, the smallest dimension is found in the case of pure and L\_PCE102–2 added C–S–H (6.2–6.4 nm) where the silicate chain length is minimum (8–9 Å), while the maximum dimension is encountered with L\_PCE23–2, which is also characterized by the longest silicate chain found in this series of samples. Gels with L\_PCE23–6 and L\_PCE102–6 lie in the middle having a silicate chain of about 10 Å and a corresponding globule dimension of 7–8 nm. This result highlights the hierarchical nature of C–S–H gel where the building block (the silicate chain) influences the size of the globule and eventually the fractal dimension of the overall

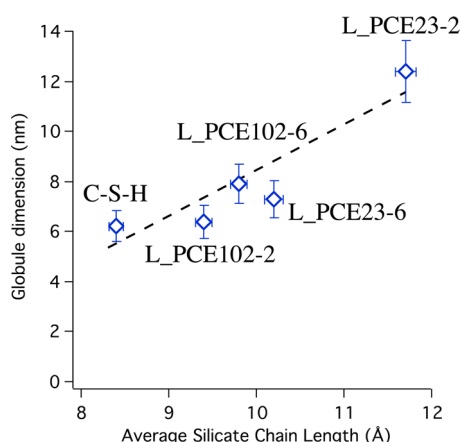
globular arrangement. Roughly 7–8 silicate chains are needed to span the entire globule diameter. At the moment the globule dimensions have not been measured for the series H, and no comparison can be done in this specific case. However considering the good correlation present in the series L, globules greater than or similar to L\_PCE23–2 are expected to be present in the C–S–H gels synthesized with a higher concentration of PCE polymers. The only exception is encountered in the case of H\_PCE102–2 where the silicate chain length is only 10.8 Å and a globule with a dimension similar to sample L\_PCE23–6 is expected. As already shown in the L series, even at high concentration the polymer PCE102–2 has the smallest propensity in changing the molecular structure of the C–S–H phase. This result is strictly related to the fact that PCE102–2 has the lowest adsorption ability in the series of superplasticizers used in the present investigation.

## CONCLUSIONS

This <sup>29</sup>Si SS-NMR study coupled with FTIR findings showed that the organic additives delay the hydration of tricalcium silicate and affect the nanostructure of the calcium silicate hydrate. The retardation effect in the hydration process is evident from the persistence of the  $Q^0$  signals in the <sup>29</sup>Si spectra of C–S–H produced in the presence of PCE and is in agreement with the previous literature. Our study shows for the first time, that the C–S–H formed in the presence of PCEs has a degree of polymerization higher than the one obtained in pure water, meaning that PCEs induce the formation of silicate chains longer than those of the plain sample. Both the retardation and the increment of DP are dependent on the molecular architecture of the PCEs: in general, they increase with the increasing of the charge density of PCE, which corresponds to the increase of the adsorption propensity: abundant and long side chains hinder the interaction of the additive with the inorganic particles; however, PCEs with short and scarce side chains easily adsorb the inorganic particles, slowing down the hydration and consequently lowering the reactivity. For these reasons, the effects are maximal in the presence of the PCE23–6 additive, which is characterized by a small density of short side chains. However, the scarcest organic–inorganic interactions occur with PCE102–2 (characterized by long side chains and high side chains density), which shows DP and reactivity values very close to those of unmodified C–S–H. PCE concentration also plays an important role, as we observe that the effects on reactivity and DP increase with increasing the amount of PCE. These results show that a combined <sup>29</sup>Si SS-NMR, FT-IR, SANS/



**Figure 8.** FTIR spectra for the investigated samples (A) at low PCE concentration and (B) at high PCE concentration. Data have been arbitrarily shifted along the y-axis for the sake of clarity.



**Figure 9.** Equivalent C–S–H globule diameter as a function of the average silicate chain length in the case of the L series. The pure C–S–H case is reported for comparison (first point on the left).

SAXS investigation can provide a very detailed picture of the nanostructure formed in the presence of additives, allowing the understanding at the supramolecular level of the C–S–H/polymer interaction that is fundamental in the design of novel performing additives for cement-based building materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

Differential thermograms of all C–S–H/PCE samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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