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Impact of Molecular Structure on Zeta Potential and Adsorbed Conformation of α -Allyl- ω -Methoxypolyethylene Glycol - Maleic Anhydride Superplasticizers

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Abstract

α -Allyl- ω -methoxypolyethylene glycol - maleic anhydride copolymers were synthesized with side chain lengths n_{EO} from 0-130 and characterized by aqueous GPC. A representation of their molecular conformation (e.g. worm-, brush- or star-like polymers) was developed. The amount of polymer adsorbed on cement rapidly decreases with increasing side chain length n_{EO} . Zeta potential measurements using the electroacoustic method in cement paste with $w/c = 0.5$ indicate that worm-like copolymers with $n_{EO} \leq 7$ adsorb flat ("train" type) and form a densely packed, thin polymer film. In this case, the adsorbed amount of copolymer is high. For star polymers with $n_{EO} \geq 34$, preferred orientation of the polymer main chain is perpendicular to the cement surface ("tail" type). The result is a thick polymer layer, with a second electrochemical double layer on top. For star polymers, the adsorbed amount is low because of the higher surface occupancy of horizontally layered side groups.

1 Introduction

Concrete flowability is greatly enhanced by the addition of polymeric dispersants (Aïtcin 1994, Ramachandran 1998). To understand the dispersing mechanism of superplasticizers, it is important to investigate the adsorption behaviour and conformation of the adsorbed polymer. It is known that the adsorbed conformation is influenced by molecular mass, side chain density and anionic charge density of the polymer as well as the ionic strength of the liquid phase (Biesalski 2002, p.39-63). Through variation of these parameters, different adsorbed conformations can be obtained. The mechanism of the adsorption of polymers in a cement slurry is very complex. For this study, polycarboxylates (PCE) based on α -allyl- ω -methoxy polyethyleneglycol-maleic anhydride copolymers were used. In contrast to superplasticizers based on methacrylic acid / ω -methoxy polyethyleneglycol methacrylate ester copolymer, they possess a well defined primary structure of alternating monomer units (ABAB) because neither maleic anhydride nor allyl ether monomer undergoes homopolymerization (O'dian 1991, p.489; Brandrup 1998, p.268). Allyl ether copolymers were synthesized with different side chain lengths (number of ethylene oxide units, n_{EO}) of the allyl ether monomer, resulting in macromolecules with worm-, brush- and star-like conformation. The correlation between molecular structure of the copolymers and their zeta potential as well as the adsorbed conformation on cement was studied.

2 Materials and methods

2.1 PCE preparation

Allyl alcohol and six different α -allyl- ω -methoxy polyethylene glycol ethers with side chain lengths of 7, 10, 34, 70, 90 and 130 ethylene oxide units (n_{EO}) were used for bulk radical copolymerisation with maleic anhydride. The molar ratio of the allyl compound to maleic anhydride was chosen as 1:1. Benzoyl peroxide was used as initiator. The initiator concentration was 1.43 M.-% in respect to the allyl compound. For copolymer preparation, maleic anhydride and the allyl monomer were added to the reaction vessel and heated to 70°C under stirring. A nitrogen blanket was applied. When reaching 70°C, the initiator was added to the mixture constantly over two hours. After further heating of the mixture for two hours, the synthesized copolymer was diluted with water. The resulting polymer solutions were neutralized with sodium hydroxide. The copolymer solutions show solids contents between 15-40 wt-% and are colorless or yellow. The chemical structures of the prepared copolymers are shown in Fig. 1.

2.2 Cement

Ordinary Portland cement (OPC) type CEM I 32.5 R obtained from Rohrdorfer Zementwerke, Rohrdorf (Germany) was used to perform spread flow, adsorption and zeta potential measurements. The composition of the pure cement was determined by Rietveld analysis as follows: 54.6 % C_3S , 20.6 % C_2S , 6.1 % C_3A cubic, 2.8 % C_3A orthorhombic, 8.5 % C_4AF , 1.7 % free CaO , 2.2 % $CaSO_4 \cdot 1/2H_2O$, 2.4 % $CaSO_4$. Its Blaine value was 3280 cm^2/g .

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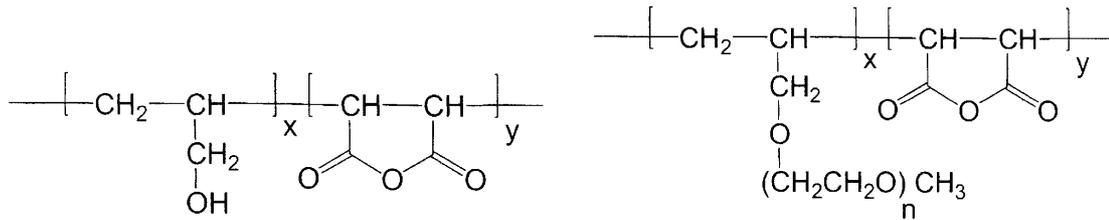


Fig. 1 Chemical structures of synthesized allyl alcohol and α -allyl- ω -methoxy polyethylene glycol maleic anhydride copolymers.

2.3 Methods

All synthesized allyl ether copolymers were characterized by a 2695 GPC separation module (Waters) containing a 2414 RI-detector (Waters) and a Dawn EOS 3 angle light scattering detector (Wyatt Technology). Ultrahydrogel columns 500, 250, 120 (Waters) with an operating range (PEO/PEG) of $M_w=100$ to 1.000.000 Da were used. 0.1 n NaNO₃ at a pH-value of 12 was used as eluent.

The zeta potential was determined with Model DT-1200 Electroacoustic Spectrometer (Dispersion Technology, Inc.). This instrument was chosen because it allows to measure zeta potentials of highly solids loaded liquids. Only such condition is similar to mortar or concrete. CEM I 32,5 R was used to prepare the cement paste. First, the ionic background of the cement filtrate was determined at a w/c ratio of 0.5. The ionic background was subtracted from the zeta potential value obtained during copolymer titration to the paste (Dukhin 2002, p.206-207; Hunter 1993, p.231-235). Aqueous copolymer solutions with 10 wt-% polymer (pH = 7) were added stepwise to the cement slurry. The zeta potential of the paste was measured as a function of copolymer dosage.

To determine the amount of adsorbed polymer, different dosages of polymer were added to the cement paste at a w/c ratio of 0.5 and stirred for 3 minutes. After 10 minutes of centrifugation at 8000 rpm, the cement filtrate was collected. Its carbon content was determined via High TOC II analyser (Elementar).

3 Results and discussion

3.1 Properties and molecular structure of PCE

From GPC measurements, the characteristic properties of the copolymers such as molar mass (M_w , M_n , M_z), polydispersity and hydrodynamic radius (R_h) were obtained. The data is shown in Table 1. As an example, the GPC spectrum of the allyl ether copolymer with $n_{EO}=10$ is shown in Fig. 2.

The main chain lengths of the copolymers were calculated based on the number average molecular weight

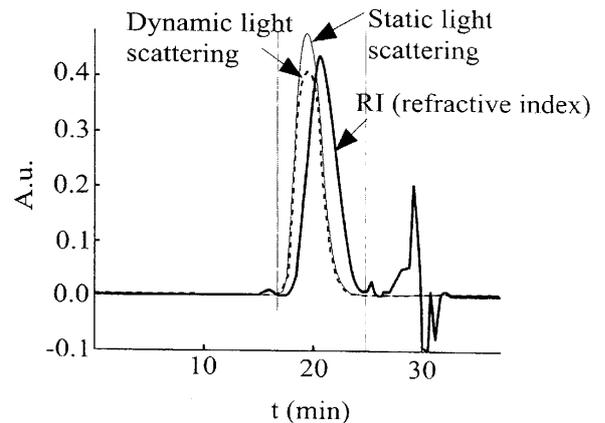


Fig. 2 GPC spectrum of allyl ether copolymer with $n_{EO}=10$.

Table 1 Properties of the synthesized copolymers.

Copolymer n_{EO}	solids content [%]	M_w [Da]	M_n [Da]	Polydispersity M_w/M_n	R_h [nm]
0	17.21	34,900	10,010	3.49	6.5
7	15.21	39,800	15,590	2.55	5.8
10	16.79	53,670	19,130	2.81	6.1
34	19.12	76,720	17,650	4.35	8.3
70	42.68	156,700	42,460	3.69	12.5
90	17.32	188,900	38,300	4.93	14.4
130	21.37	167,600	44,060	3.80	13.7

(M_n) obtained for each polymer. The molar mass of a hypothetical unit (M_u) comprising of one mol of maleic anhydride and one mol of the allyl compound was calculated by adding the masses of all atoms in the unit. The repeat number n of the hypothetical unit was determined by dividing M_n by M_u . The main chain length was obtained by multiplying the average backbone length of M_u which is 2×0.252 nm with the repeat number n . This calculation is based on a C-C-C length of 0,252 nm and assumes that the polymer chain is ideally stretched. The calculation of the different side chain lengths is based on the assumption of a helical structure of the ethylene oxide units. According to this model, a side chain length of $n_{EO} = 7$ exhibits a length of 1.95 nm (Ohta 2000).

Figure 3 shows the calculated main and side chain lengths for all copolymers. Copolymers with $n_{EO} \leq 10$ have a longer main than side chain, whereas for $n_{EO} \geq 34$ the side chain is longer than the main chain.

The solution structure of comb polymers can be classified in five different groups, depending on main chain length, side chain length and side chain density of the polymers (Borget 2005). Figure 4 shows a plot of side

chain length (n_{EO}) versus main chain length (n) as proposed by GAY *et al.* (2001, p.229-236). $N = 2$ is the number of monomers per unit along the backbone. According to this model, comb polymers can assume the secondary structure of a decorated chain (DC), a flexible backbone worm (FBW), a stretched backbone worm (SBW), a stretched (SBS) or a flexible backbone star (FBS) (Gay 2001). Application of this model to the synthesized copolymers results in the structures as follows: The allyl alcohol copolymer is a worm-like, flexible molecule without side groups. The allyl ether copolymer with $n_{EO} = 7$ possess a flexible backbone worm (FBW) structure ($n_{EO} < N^3$). In between different main chain segments, the backbone is flexible. For medium long side chains ($n_{EO} = 10-34$), the copolymers are represented by the stretched backbone worm (SBW) model. Within this regime, the backbone consists of a number of stretched main chain segments. Copolymers with even longer side chains ($n_{EO} \geq 70$) resemble star molecules. Their long side chains spread away in all directions of the small and completely stretched backbone found in the core region of the molecule. The synthesized allyl ether copolymers with $n_{EO} = 70-130$ belong

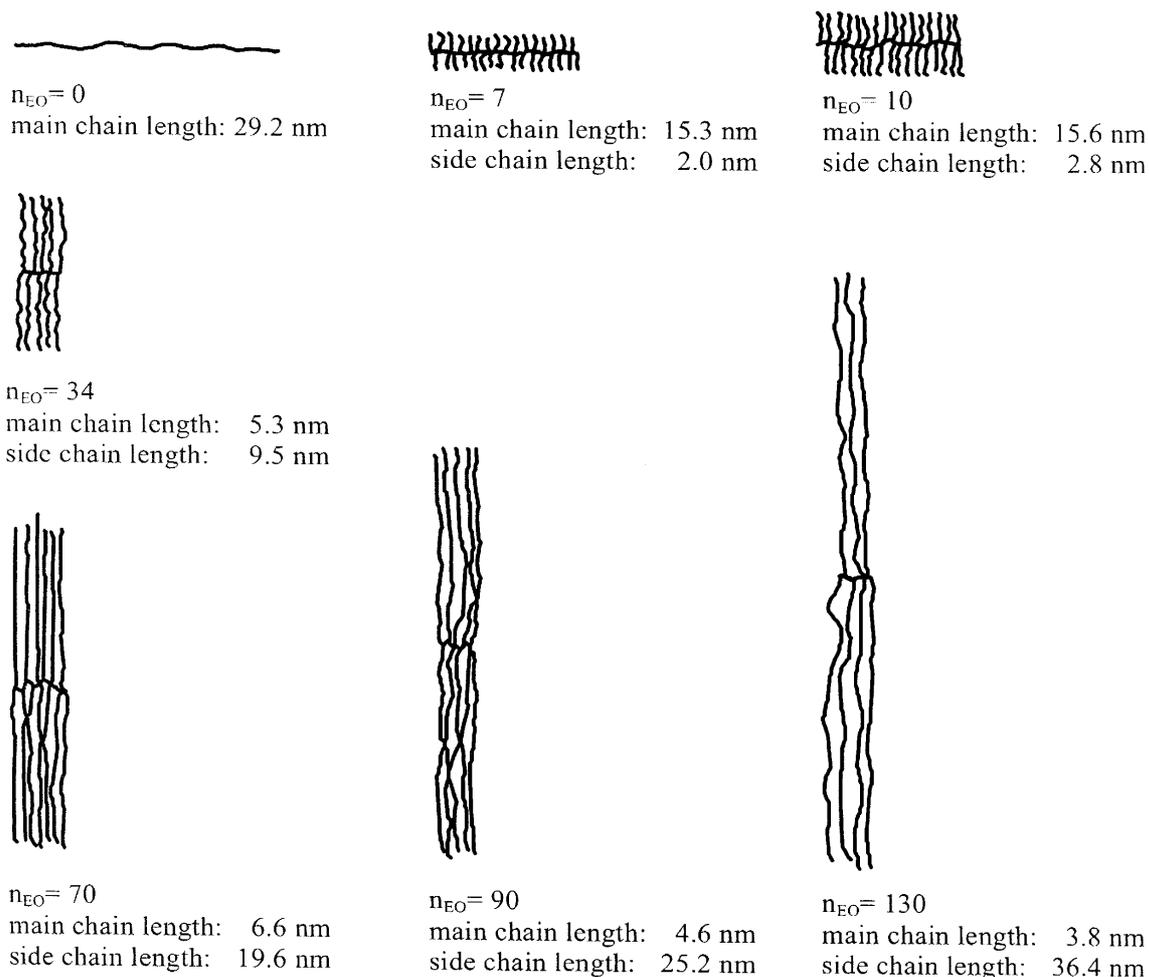


Fig. 3 Schematic representation of calculated main and side chain lengths of allyl alcohol and allyl ether copolymers.

to the stretched backbone star (SBS) regime.

3.2 Dispersing effect of allyl copolymers

The dispersing capability was measured by using the mini slump test as follows: A cement paste was prepared by mixing 300g OPC (CEM I 32.5 R) at $w/c = 0.475$ for 2 minutes and filled evenly into a Vicat ring which was lifted to yield a spread flow of 18 ± 0.5 cm. For each superplasticizer, the required dosage to increase the spread to 26 ± 0.5 cm was determined. The result is shown in Fig. 5. All synthesized polycarboxylates are highly efficient superplasticizers and require dosages of 0.1 to 0.3 M-% by weight of cement. Copolymers with short side chains ($n_{EO} \leq 34$) are particularly effective.

3.3 Adsorption behaviour

The amount of copolymer adsorbed on cement CEM I 32,5 R was determined for each sample. All allyl ether PCEs show LANGMUIR-type adsorption isotherms. Also, with increasing side chain length, the maximum adsorbed amount of polymer decreases. The longer the side chain, the lower the amount of allyl ether copolymer required in order to obtain a saturated layer of adsorbed polymer. As an example, Fig. 6 illustrates the adsorption isotherms of three copolymers with side chain lengths of $n_{EO} = 7$, $n_{EO} = 34$ and $n_{EO} = 130$.

For α -allyl- ω -methoxy-polyethylene glycol - maleic anhydride-styrene terpolymers, similar results on adsorbed amounts were reported earlier by SAKAI *et al.* Based on their data, they proposed that the decline of the saturated amount of adsorbed polymer observed with increasing side chain length might be attributed to a change in the conformation of the adsorbed comb polymers (2003a, p.16-25). Other authors observed that the adsorption rate of PCE decreases with increasing side chain density or lower anionic charge density. The reason being that a polymer backbone with high amount of negatively charged anchor groups sterically is less hindered for adsorption on the binder surface (Li 2005, Uchikawa 1995).

3.4 Zeta potential measurements

Zeta potential measurements of cement pastes are an effective method to investigate the dispersing mechanism of a superplasticizer. A strong decline of the zeta potential to more negative values indicates electrostatic repulsion between cement particles. They become more negatively charged due to adsorbed superplasticizer molecules. On the other hand, if the zeta potential changes only slightly during superplasticizer addition, steric hindrance between the cement particles carrying adsorbed polymer molecules is the main mechanism for dispersion. The value of the zeta potential not only depends on polycarboxylate adsorption, but also on the progress of cement hydration which may result in different concentrations of ions (especially Ca^{2+} and SO_4^{2-}) in the pore solution over time.

To investigate the impact of cement hydration, the

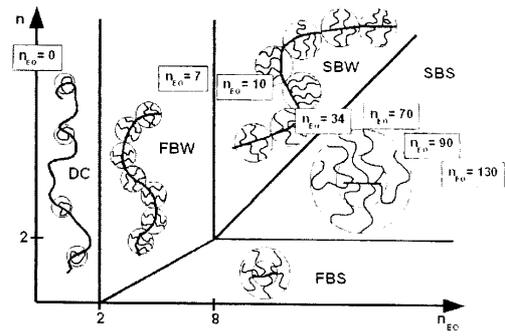


Fig. 4 Solution structure of the synthesized allyl copolymers, classified according to GAY. (2001, p.229-236)

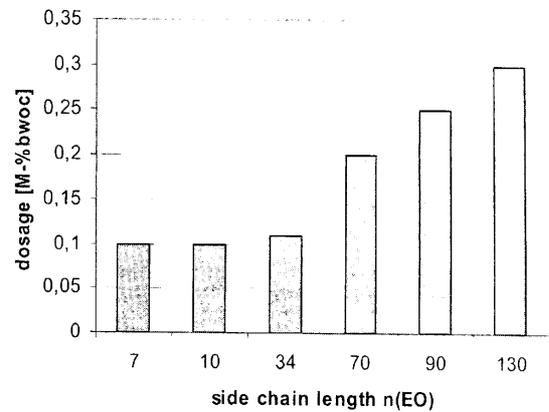


Fig. 5 Required dosage (by weight of cement) of allyl ether copolymers to obtain a cement paste spread of 26 ± 0.5 cm.

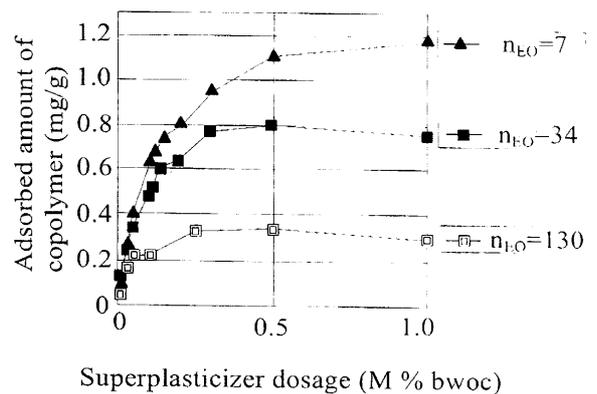


Fig. 6 Adsorption isotherms of selected allyl ether copolymers.

zeta potential of the cement paste without superplasticizer was measured over time. No change of the initial zeta potential value of -5.8 mV during the first hour after preparation of the cement slurry was observed. The initial Ca^{2+} concentration in the cement filtrate was 1100

mg/l. It did not change notably over the first 30 minutes. Thus, it was concluded that during the first hour the zeta potential is only influenced by superplasticizer adsorption. To investigate on the dispersion mechanism for the allyl copolymers ($n_{EO} = 0, 7, 10, 34, 70, 90, 130$), their zeta potentials in cement paste were measured at increasing dosages. The results are shown in Fig. 7.

All samples except for the allyl alcohol copolymer, increase the zeta potential to more positive values. Therefore, the effect of sterical hindrance for dispersion was confirmed. Further, when the side chain length n_{EO} of the copolymers was ≥ 10 , even positive zeta potentials were observed. To explain this unexpected effect, the molecular conformation and orientation of the adsorbed macromolecules was studied. When PCE comb polymers adsorb on a binder surface, the shear plane between the STERN layer and the diffuse layer can shift to greater distance from the cement grain surface (Plank 2005). Structural properties of the polymer such as side chain length, side chain density and anionic charge density determine both the location of the shear plane and the conformation of the adsorbed macromolecule.

It has been reported that the anionic charge density of polycarboxylates decreases with increasing side chain length (Sakai 2003b). This effect can be demonstrated e.g. by charge titration experiments. As the main chain length of the synthesized allyl ether copolymers decreases with increasing n_{EO} , the number of carboxylic groups per molecule is decreasing as well. Thus, comb-type polymers with short side chains and high anionic character can be expected to adsorb flat on the cement surface due to their higher anionic charge density whereas molecules with long side chains should prefer perpendicular orientation of the main chain. Different adsorbed conformations will produce different zeta potentials. According to the results obtained from zeta potential measurements, the allyl copolymers can be classified into 3 groups, as shown in Fig. 8:

Case 1:

The linear allyl alcohol - maleic anhydride copolymer increasingly adsorbs with increasing dosage until it reaches a saturation point in the adsorbed amount at around 0.3 wt-% dosage. With increasing adsorption, the zeta potential becomes more negative. Electrostatic repulsion is responsible for dispersion.

Case 2:

Allyl ether copolymers with side chains of $n_{EO} < 10$ cause an increase of the zeta potential to less negative values, but still below the iso electric point. This behaviour is explained by the steric effect of their side chains which move the shear plane of the zeta potential further away from the particle surface (Plank 2005). Thus, steric hindrance is the main mechanism for dispersion.

Case 3:

Allyl ether copolymers with side chains of $n_{EO} \geq 10$ cause a positive zeta potential. The explanation for the change in the sign of the zeta potential is the formation of a second electrochemical double layer on top of the

adsorbed polymer layer. This is only possible if the main chain of the macromolecule adsorbs perpendicular to the binder surface. In this case, sufficient anionic charge will exist on the surface of the polymer layer to allow further adsorption of Ca^{2+} ions.

It also was puzzling that zeta potentials are most positive for copolymers with $n_{EO} = 34$ and start to decrease when longer side chains are present. This effect is explained by the differences in the secondary molecular structure of the copolymers. It is shown schematically in Fig. 9.

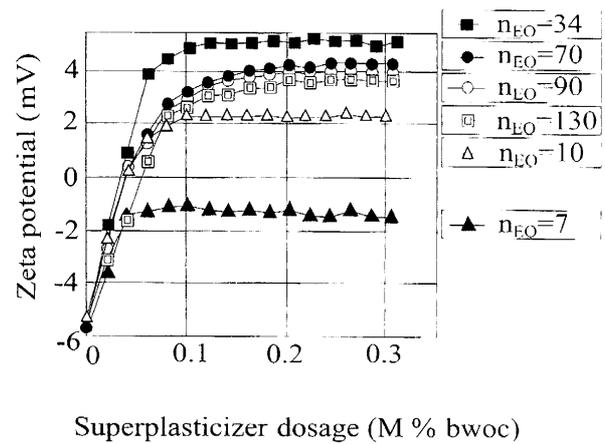


Fig. 7 Zeta potential of allyl ether copolymers.

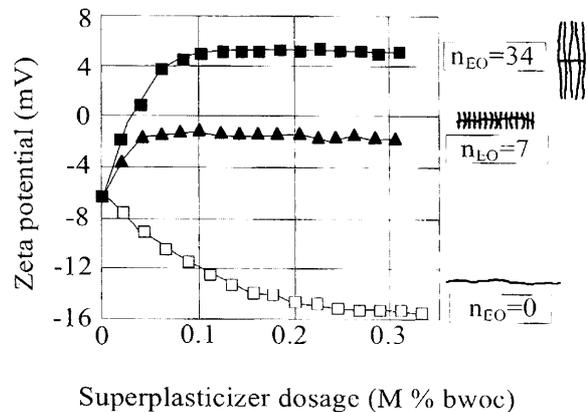


Fig. 8 Zeta potential and molecule structure of allyl alcohol and allyl ether copolymers with side chain lengths of $n_{EO}=7$ and 34.

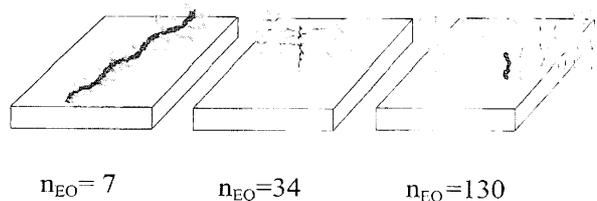


Fig. 9 Adsorbed conformation of allyl ether copolymers on the cement grain having side chain lengths of $n_{EO}=7, 34$ and 130 ethylenoxide units.

According to the results of zeta potential measurements, allyl copolymers belonging to the groups of decorated coils or flexible backbone worms ($n_{EO} < 8$) adsorb flat on the cement surface. They form a densely packed polymer film with macromolecules being stacked parallel side by side. Hence, the adsorbed amount can be very high. On the other hand, the main chain of stretched worm or star molecules of the allyl ether copolymers ($n_{EO} = 10-130$) adsorbs perpendicular on the cement surface. The result is a polymer layer containing less amount of polymer because of the higher surface occupancy of the side groups. The allyl ether copolymer with $n_{EO} = 34$ produces the most positive zeta potential. The reason being that, in contrast to the copolymer with $n_{EO} = 130$, it consists of a longer main chain, carrying more negative charges, and the shorter side chains, requiring less space on the particle surface. Thus, it attracts more Ca^{2+} ions in the second electrochemical double layer than the allyl ether copolymer with $n_{EO} = 130$. A schematic representation of the different adsorbed conformations of allyl ether copolymers with $n_{EO} = 7$; 34 and 130 on the STERN layer of a hydrating cement particle and the resulting zeta potentials are given in Fig. 10.

4 Conclusions

Allyl ether – based PCE superplasticizers adsorb in different conformation on the cement surface, depending on their molecular structure. Decorated coils or flexible

backbone worms are obtained when n_{EO} is at or below 7. They adsorb flat in high amount and form a densely packed polymer film. Stretched backbone worms or star-like molecules with n_{EO} at or greater than 10, adsorb perpendicular on the surface. Their adsorbed amount is smaller because the steric effect of their side chains prevents a dense packing of molecules on the surface.

Results obtained from zeta potential measurements allow a better understanding of the nanoscopic architecture of polymer layer on a hydrating cement grain if the secondary structure of the PCE molecule is known. Information concerning the polymer film is highly important because the adsorbed orientation of the PCE molecule greatly impacts the dosage required to achieve a certain flowability of concrete. It can be expected that a thorough understanding of the adsorbed polymer layer will lead to concepts with improved PCE structures, capable of more efficient dispersion.

Acknowledgement

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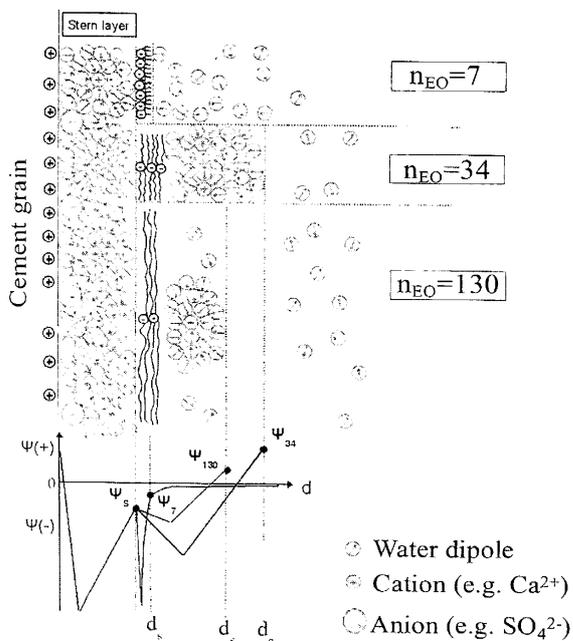


Fig. 10 Schematic representation of the adsorbed conformation of allyl ether copolymers with side chain lengths of $n_{EO} = 7$; 34 and 130 adsorbed on the STERN layer of hydrating cement particle, as derived from zeta potential measurement.

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