Cement and Concrete Research 84 (2016) 20–29

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

A microstructural analysis of isoprenol ether-based polycarboxylates and the impact of structural motifs on the dispersing effectiveness

Johann Plank [a,*], Huiqun Li [a,b,d], Manuel Ilg [a], Julia Pickelmann [a], Wolfgang Eisenreich [c], Yan Yao [d], Ziming Wang [b]

[a] Technische Universität München, Chair for Construction Chemistry, 85747 Garching, Lichtenbergstraße 4, Germany
[b] Beijing University of Technology, College of Materials Science and Engineering, 100124 Beijing, China
[c] Technische Universität München, Chair for Biochemistry, 85747 Garching, Lichtenbergstraße 4, Germany
[d] China Building Materials Academy, State Key Laboratory of Green Building Materials, 100024 Beijing, China

ARTICLE INFO

Article history:
Received 7 August 2015
Accepted 17 February 2016
Available online 14 March 2016

Keywords:
Admixture (D)
Microstructure (B)
^{13}C NMR spectroscopy (B)
Polycarboxylate superplasticizer
Polymers (D)

ABSTRACT

Generally, polycarboxylate superplasticizers (PCEs) are synthesized via aqueous free radical copolymerization. The conditions during copolymerization such as relative reactivity and feeding mode and ratio of monomers can cause different monomer sequences in the final product. In this study, the sequence of monomers in PCE polymers synthesized from acrylic acid and isoprenyloxy polyethylene glycol (IPEG) macromonomer was characterized by ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Three different triads of monomer sequences (EAE, AAE and AAA; E = ether, A = acid monomer) were detected. It was found that IPEG PCEs predominantly contain the structural motifs of AAE and EAE, and less of AAA. Higher additions of acrylic acid do not incorporate into the structure of PCE, but convert to HMW polyacrylate as by-product instead. A PCE with optimal dispersing effectiveness was achieved at high contents of IPEG macromonomer, a molecular weight (M_w) around 40,000 Da and narrow molecular weight distribution.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polycarboxylate superplasticizers (PCEs) have become an essential admixture for the concrete industry since their invention in 1981 [1]. They can significantly improve fluidity, compressive strength and durability of concrete [2,3]. The designable structure of PCE endows them various preferential properties arising from specific microstructures.

It is known to those skilled in the art that in PCE copolymers, the feeding molar ratios of the macromonomers do not necessarily represent the actual molar ratios present in the final product. In fact, when combining such highly reactive monomers like acrylic acid or methacrylic acid with macromonomers, then copolymers of non-homogeneous composition are formed. In aqueous radical copolymerization the monomers can arrange randomly, alternating, in block or in graft chains. An overview of the different possibilities existing for a system composed of two monomers, A and B respectively, is shown in Fig. 1.

The sequence of monomers in copolymers can be predicted by the value of the monomer reactivity ratios. If the value of r_1 is higher than 1, then A tends to react with itself, thus forming a homopolymer or – in the case of two monomers – a block copolymer. For example, if r_1 is greater than 1 and r_2 less than 1, then a copolymer with blocks as shown in Fig. 2 is formed [4].

Exactly this situation occurs when acrylic acid and isoprenyloxy polyethylene glycol (IPEG) macromonomer are copolymerized, as it is well established that the reactivity of acrylic acid is much higher than that of the IPEG macromonomer [5]. Obviously, it is highly desirable to understand the actual sequence of monomers present in a synthesized PCE copolymer, as it may directly affect its adsorption behavior and dispersing power in cement paste. Thus, a suitable analytical method allowing precise determination of the monomer sequence in a PCE copolymer is most essential.

^{13}C NMR spectroscopy reflects the resonance of the ^{13}C nucleus to the external magnetic field which is affected by the electron density in the proximity. Thus, in a certain functional group the resonance of the ^{13}C nucleus varies with different neighboring monomers connected. This effect has been utilized to determine the monomer sequences present in methacrylate ester copolymers [6,7] and in hydrolyzed polyacrylamides [8]. Relative to PCEs, *Belloto* and *Rozzoni* have applied this method to methacrylate ester (MPEG)-based PCEs and revealed interesting details on the microstructural composition of these copolymers [9]. In the present study, this method was applied to analyze specifically synthesized IPEG PCE copolymers with the aim to compare the actual monomer sequence with that derived statistically from the molar feeding ratios.

---

* Corresponding author. Tel.: +49 89 289 13151; fax: +49 89 289 13152.
E-mail address: sekretariat@bauchemie.ch.tum.de (J. Plank).

http://dx.doi.org/10.1016/j.cemconres.2016.02.010
0008-8846/© 2016 Elsevier Ltd. All rights reserved.

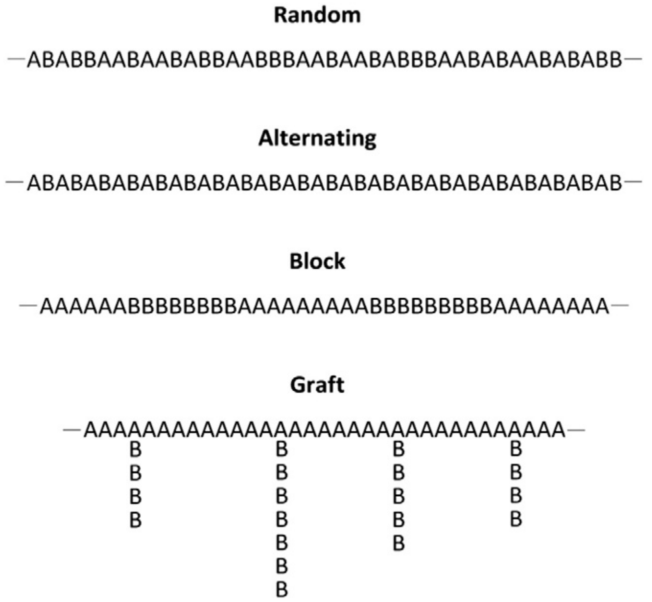

Fig. 1. Potential monomer sequences formed in free radical copolymerization of two monomers, A and B.

Theoretically, and assuming that the PCE polymer is prepared at a molar excess of acrylic acid over the IPEG macromonomer, then the monomer sequences expressed as triads as shown in Fig. 3 can occur in the PCE polymers. Note that sequence EEE was considered as unlikely and therefore excluded on the grounds of the relatively lower concentration and reactivity of the macromonomer compared to acrylic acid, as will be shown later. Similarly, AEA which presents a variation of the structural motif AAE was not considered here because later in the evaluation of the ^{13}C NMR spectra, no indication for occurrence of this monomer sequence was found.

The goal of this study was to determine the microstructure of four different IPEG PCE samples synthesized at varied molar ratios of acrylic acid to macromonomer (1:1, 2:1, 3:1 and 4.5:1) at a constant side chain length of 9 EO units in the macromonomer. Moreover, size exclusion chromatography (SEC) was applied to characterize the molecular properties and residual amounts of non-reacted IPEG macromonomer or acrylic acid homopolymer present in the final product.

PCE molecules can disperse cement particles effectively based on the combined effects of electrostatic repulsion and steric hindrance (an “electrosteric” effect) [10,11]. The sequence of monomers reflects the arrangement of the anchor and the pendant groups present in the PCE polymers. Apparently, such arrangement can have significant effect on the dispersing effectiveness of a PCE product. Therefore, the dispersing power of the synthesized copolymers was determined by using a mini slump test involving cement paste. The results were correlated with those obtained from the microstructural analysis, and a model was sought which can identify the microstructure which is optimal for the dispersion of cement.

2. Materials and experiments

2.1. Materials

The macromonomers isoprenyloxy polyethylene glycol ether with $M_w = 500$ Da and 1100 Da (abbreviated as IPEG-500 and IPEG-1100) containing 9 and 25 ethylene oxide units, respectively, were provided by Clariant Deutschland GmbH, Burgkirchen, Germany. These short-chain macromonomers were chosen to ensure a high content of the trigger carbon atoms in acrylic acid and IPEG macromonomer which is essential for the accuracy of the results from ^{13}C NMR spectroscopy. Sodium polyacrylate (Sokalan® PA 40) with a degree of polymerization (DP) of 40 was provided by BASF SE, Ludwigshafen, Germany. Acrylic acid, ammonium persulfate and sodium methyallyl sulfonate were all purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used as is.

For the dispersing tests, a CEM I 52.5 N (Milke® Classic from HeidelbergCement, Geseke plant, Germany) was used. Its phase composition determined by quantitative X-ray diffraction including *Rietveld* refinement (Bruker axs D8) is shown in Table 1. Its average particle size (d_{50} value) was found at 11.5 μm (laser granulometer Cilas 1064, Cilas, Marseille, France) and its specific surface area (*Blaine* instrument, Toni Technik, Berlin, Germany) was 5383 cm^2/g.

2.2. Synthesis of PCE copolymers

A series of polycarboxylate superplasticizers with different molar ratios of acrylic acid to IPEG was synthesized by aqueous free radical copolymerization. The polymers were designated as xIPEGy.0, whereby x represents the degree of polymerization of ethylene oxide in the macromonomer; while y represents the molar ratio of acrylic acid to the macromonomer. Ammonium persulfate was used as initiator and sodium methallyl sulfonate as chain transfer agent. As an example, the preparation of 9IPEG2.0 polymer is described: 50.0 g of IPEG-500 macromonomer was dissolved in 80.0 g DI water and placed in a five neck round bottom flask with a mechanical stirrer and heated to 60 °C using a water bath. Then 14.4 g acrylic acid and 4.74 g of sodium methallyl sulfonate were dissolved in 15.0 g DI water. This mixture was designated as solution A. Next, 3.87 g of ammonium persulfate was dissolved in 15.0 g DI water and labeled as solution B. Solution A and B were fed separately and continuously into the reaction flask over a period of 3 h, followed by post treatment for 2 h at 60 °C. The reaction mixture was cooled to ambient and adjusted from pH ~ 1.5 to 7.5 with aqueous 30 wt.% NaOH solution, yielding a yellowish aqueous PCE solution with a solid content of 39 wt.%.

2.3. Size exclusion chromatography (SEC)

PCE solutions of 10 g/L concentration were used in the size exclusion chromatography (SEC) measurements. A Waters 2695 Separation Module equipped with three Ultrahydrogel™ columns (120, 250, 500) and a Ultrahydrogel™ guard column from Waters, Eschborn, Germany, and a three angle static light scattering detector (“mini Dawn” from Wyatt Technology Corp., Santa Barbara, CA, USA) was used in the measurements. Polymer concentration was recorded with a differential refractive index detector (RI 2412, Waters, Eschborn, Germany). Molecular weight, polydispersity index and hydrodynamic radius of the PCE polymers were obtained from the light scattering detector. As eluent, 0.1 N $NaNO_3$ adjusted to pH 12.0 pumped at a flow rate of 1.0 mL/min was used. For calculation of M_w and M_n a value of dn/dc of 0.135 mL/g (the value for polyethylene glycol) was adopted [12].

2.4. ^{1}H and ^{13}C NMR spectroscopic analysis

^{1}H NMR spectroscopy was used to calculate the actual molar ratio of monomers present in the synthesized PCE polymers. For these measurements, an AVANCE-III 400 MHz NMR spectrometer (Bruker BioSpin

Fig. 2. Sequence of monomers A and B in a copolymer obtained when $r_1 > 1$ and $r_2 < 1$.

Download English Version:

https://daneshyari.com/en/article/1455978

Download Persian Version:

https://daneshyari.com/article/1455978

Daneshyari.com