Chromatographia (2011) 73:1131–1136
DOI 10.1007/s10337-011-2015-5

ORIGINAL

# RP-LC Determination of Residual Monomers in Polycarboxylate Superplasticizers

**Jiaheng Lei · Xiaodi Du · Anfu Zhang · Hui Wu**

Received: 8 January 2011 / Revised: 24 February 2011 / Accepted: 18 March 2011 / Published online: 30 April 2011


**Abstract** A procedure was developed for the determination of residual monomers in polycarboxylate superplasticizer by reversed-phase high performance liquid chromatography. Seven kinds of residual monomers were quantitatively determined on a SinoChrom ODS-BP (C18) column and UV detector at 205 nm. The mobile phases which were used to determine micromolecular monomers were composed of acetonitrile and phosphate buffer solution (0.05 mol $L^{-1}$, pH = 3) in the ratio of 8:92 (*v*/*v*). While the mobile phases for long side-chain monomers testing were composed of acetonitrile and phosphate buffer solution (0.05 mol $L^{-1}$, pH = 6.5) in the ratio of 40:60 (*v*/*v*). The linear response ranged from $4.0 \times 10^{-6}$–$2.0 \times 10^{-3}$ mol $L^{-1}$. The detection limit was $0.12 \times 10^{-5}$–$0.8 \times 10^{-5}$ mol $L^{-1}$. Determination of real samples showed that relative standard deviation of high conversion rate samples was 3.1–8.7% and standard addition recovery ratio was 91.5–102.8%. While the relative standard deviation of low conversion rate samples was less than or close to 1% and the standard addition recovery ratio was 96.3–103.1%.

**Keywords** Column liquid chromatography · Polycarboxylate superplasticizer · Residual monomer · Concrete admixture

## Introduction

Polycarboxylate superplasticizers (PCs), a wide variety of polyfunctional polyelectrolytes, play an important and irreplaceable part in modern concrete [1, 2]. Normally, PCs can be prepared by copolymerization of monomers with different functional groups which include carboxylic acid group, sulfonic acid group and long side-chain [2–6]. A variety of researches have proved that residual monomers have significant effect on performance of PCs [7–9]. At present, halogen addition oxidation reduction titration is commonly used to determine residual monomers [10]. But it is only suited to quantify the total amount of residual monomers and shows low sensitivity. In 2000, Yamada et al. [7] determined different residual monomers in reaction system by ion chromatography and gel permeation chromatography in order to calculate the average construction of polycarboxylate superplasticizers; however, PCs macromolecules might interfere with determination of monomers. Subsequently, a method for separation of macromolecules and monomers in PCs system by semi-permeable membrane techniques was reported and further studied [8, 9], but it cost a long time for separation. Reversed-phase high performance liquid chromatography (RP-LC) was reported to determine residual monomers in synthetic resin systems, such as superabsorbent polymer hydrogels [11], dental acrylic resin [12, 13] and polylactide resin [14]. However, the matrix of determination should be pretreated by extraction to avoid inference of polymerization products, which might then take a longer operating procedure and bring unexpected deviation of quantification result. Though residual monomers in resin system have been reported to be directly determined by head space gas chromatography without separation or extraction [13, 15], only volatile monomers could be determined exactly.

Typical PCs mainly include polyacrylic acid system, polymethylacrylic acid system and polymaleic acid system [16, 17], and monomers for PCs synthesis include acrylic acid (AA), methylacrylic acid (MAA), maleic anhydride

J. Lei (✉) · X. Du · A. Zhang · H. Wu
Department of Chemistry, Wuhan University of Technology, Wuhan 430070, Hubei, People's Republic of China
e-mail: yhx2000@263.net

(MA), sodium methylallyl sulfonate (MAS), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), methoxypolyethylene glycol acylate (MPEGA) and methoxypolyethylene glycol methyl acrylate (MPEGMA), etc. [2–6, 16, 17]. In this paper, chromatographic condition of each residual monomer separation by RP-LC in PCs system was studied, and a chromatographic method for residual monomers quantitative determination in PCs systems without separation was developed in accordance with strong water-solubility of PCs. The method developed was simple to carry out and had high accuracy and sensitivity, which allowed determination of seven kinds of residual monomers in different PCs systems. Besides, it could be applied to determine the reaction rate of different monomers and study polymerization kinetics.

## Materials and Methods

### Chemicals and Reagents

The HPLC analysis used AGILENT-1100 chromatography system (AGILENT Company, US). Acetonitrile as the mobile phase was chromatographic grade. Water used in this experiment was double distilled. The UV spectrum analysis used $\lambda$-35 UV spectrometer (PE Company, US). Other reagents were analytical grade. AA and MAA were purified by reduced pressure distillation. MA was purified by reduced pressure sublimation. MAS and AMPS were purified by recrystallization. MPEGA (molecular weight is 1,000) and MPEGMA (molecular weight is 1,000) were prepared according to Ref. [5] and purified by extraction with NaCl aqueous solution and ethyl acetate system.

Seven standard samples were all purchased from Sigma-Aldrich Company, USA, with purity of more than 99%. Those samples were diluted to the concentration of 0.0200 mol $L^{-1}$ by water as standard solutions, adding 0.05% hydroquinone to prevent autopolymerization. Then standard solutions were preserved in refrigerator under 4 °C. Solution of a certain concentration could be obtained by diluting with mobile phase before using.

### Chromatographic Conditions

Residual monomers were separated on a SinoChrom ODS-BP (C18) column (4.6 × 200 mm i.d., 5 μm) at 30 °C. The wavelength of UV detector was 205 nm. Mobile phases of micromolecule monomers determination composed of acetonitrile and phosphate buffer solution (0.05 mol $L^{-1}$, pH = 3) in the ratio of 8:92 (*v*/*v*). The mobile phases of long side-chain monomers determination composed of acetonitrile and phosphate buffer solution (0.05 mol $L^{-1}$, pH = 6.5) in the ratio of 40:60 (*v*/*v*). The flow rate was constant at 1.5 mL $min^{-1}$. The injection volume was 10 μL.

### Sample Preparation

This study investigated three representative systems, including the PAA system (A), PMAA system (B) and PMA system (C), of which the PCs samples were prepared according to Ref. [3–5]. Each PCs sample was accurately weighed 0.10–0.25 g and diluted to 25 mL with mobile phase, followed by a filtration through a 0.45-μm membrane filter for further use. External standard method was used to determine the samples.

## Result and Discussion

### Chromatographic Separation of Samples

In this paper, polyacrylic acid system (A), polymethacrylic acid system (B) and polymaleic acid system (C) were studied. In all these systems, seven kinds of monomers were mainly involved, including AA, MAA, MA, MAS, AMPS, MPEGA (molecular weight 1,000) and MPEGMA (molecular weight 1,000). The monomers above could be classified into three types according to their chemical structures: carboxyl group monomer, sulfonic acid group monomer and long side-chain monomer. The first two types were usually called micromolecular monomers and the last was called macromolecular monomer. Since polycarboxylate superplasticizers were synthesized by copolymerization of different monomers [16, 17], chromatographic separation results of seven monomers in mixed standard solution were investigated at the same time in order to suit the determination method to more extensive application. Impurities in monomers such as hydroquinone and toluene-*p*-sulfonic acid should be separated by chromatography. The superplasticizer mixture with no residual monomers (conversion rate higher than 99.8%) was used as blank sample to carry out a contrast experiment.

The chromatographic behavior of carboxylic monomer and sulfonic monomer were quite different from long side-chain monomers because of their strong polarity and hydrophilicity. Therefore, micromolecular monomers and long side-chain monomers could be separated and determined on RP-LC by two steps.

The chromatographic analysis results of micromolecular monomers are shown in Fig. 1. It can be seen that when using acetonitrile and phosphate buffer solution (0.05 mol $L^{-1}$, pH = 3) in the ratio of 8:92 (*v*/*v*) as mobile phase, the micromolecular monomers even impurities like hydroquinone and toluene-*p*-sulfonic acid could be separated completely on C18 column and the resolution of each

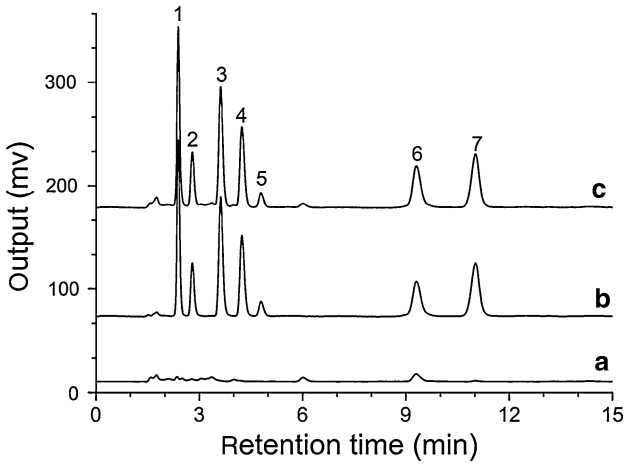


**Fig. 1** Chromatographic separation result of micromolecular monomers, including: **a** blank solution, **b** mixed standards, **c** blank sample with additional standard solution. The peaks stand for: *1* maleic acid, *2* MAS, *3* AMPS, *4* acrylic acid, *5* hydroquinone, *6* toluene-*p*-sulfonic acid, *7* methacrylic acid

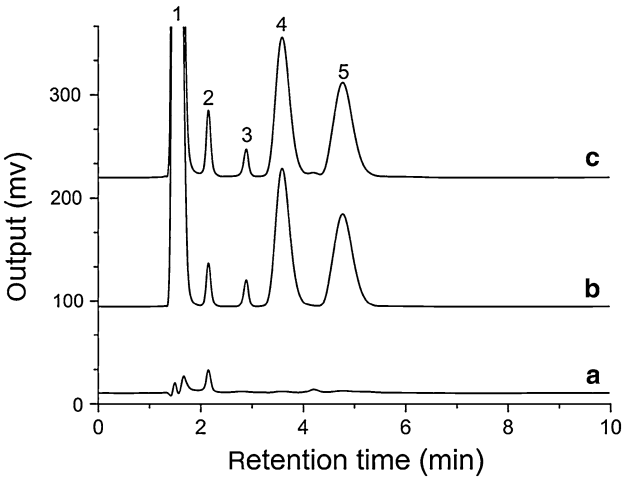


**Fig. 2** Chromatographic separation result of long side-chain monomers, including: **a** blank solution, **b** mixed standards, **c** blank sample with additional standard solution. The peaks stand for: *1* micromonomers, *2* toluene-*p*-sulfonic acid, *3* hydroquinone, *4* MPEGA, *5* MPEGMA

peak was above 1.5. As presented in Fig. 1, by comparison of chromatograms of blank solution, mixed standards, blank sample with additional standard solution, polymerization products and long side-chain monomers did not produce chromatographic peaks under the chromatographic condition. This may indicate that polymerization products and long side-chain monomers did not interfere with separation and determination of micromolecular monomers.

By using acetonitrile and phosphate buffer solution (0.05 mol $L^{-1}$, pH = 6.5) in the ratio of 40:60 (*v*/*v*) as mobile phase, long side-chain monomers could be perfectly separated on C18 column. The retention time of each micromolecular monomer and other impurities was short and close to dead time so that they did not interfere with determination of long side-chain monomers. As shown in Fig. 2, the polymerization product produced no chromatographic peak. As a result there was little interference with the separation and determination of long side-chain monomers.

Since the capacity factor changed a lot with varying temperature due to the hydrophilicity of polyethylene chain which varied with temperature [18], the separation effect of long side-chain monomers was obviously influenced by column temperature. The best separation result was obtained by controlling the column temperature at 25–30 °C. If the column temperature was too high, the shape of the peaks would broaden. While the column temperature was too low, the retention time of long side-chain monomers significantly reduced and degree of separation decreased.

## Selection of Detection Conditions

All monomers under test except MAS contained $\alpha,\beta$-unsaturated double bond which had strong UV absorption. Besides, the double bond in MAS molecular was influenced by strong inductive effect from sulfonic group and delocalization happened, which lead to lower UV absorption. Therefore, all these monomers could be detected by UV detection. The UV absorption spectra of each monomer are shown in Fig. 3. Though experimental results indicated that absorption curve of each monomer was obviously different from each other, all their signal response ranged from 190 to 220 nm in varying degrees. So this range was selected as determination wavelength to obtain significant response signals. The absorption intensity of a majority of detected monomers increased with reducing absorption wavelength. As a result, its advantageous to detect at lower wavelength to improve the signal intensity. But the signal-to-noise ratio (S/N) decreased as strong background absorption of mobile phase under the wavelength of 200 nm. It is appropriate to choose 205 nm as the detective wavelength.

## Linear Response Ranges and Detection Limits

The linear response range of this method was detected in standard solution of different concentrations and results were shown in Table 1. The results showed a good linear relationship when the concentration of MA was $1.0 \times 10^{-6}$ –$1.0 \times 10^{-3}$ mol $L^{-1}$, MAS, AMPS, AA and MAA was $2.0 \times 10^{-6}$–$2.0 \times 10^{-3}$ mol $L^{-1}$, MPEGMA and MPEG MMA was $4.0 \times 10^{-6}$–$2.0 \times 10^{-3}$ mol $L^{-1}$. And the

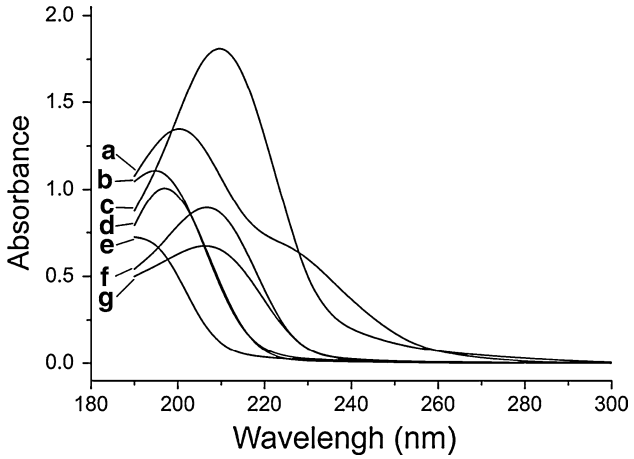


**Fig. 3** UV spectra of monomers, including: **a** AMPS, **b** AA, **c** MA, **d** MPEGA, **e** MAS, **f** MAA, **g** MPEGMA

correlation coefficients ($r^2$) of regression equations were all above 0.999. Based on S/N = 3, the detection limits of micromolecular monomers were below $0.02 \times 10^{-5}$ mol $L^{-1}$, and that of long side-chain monomers were less than $0.1 \times 10^{-5}$ mol $L^{-1}$. The detection limits of real samples decreased because of background noise increment caused by matrix interference. The detection limit of blank sample with additional standard solution was approximately $0.12 \times 10^{-5}$–$0.8 \times 10^{-5}$ mol $L^{-1}$.

### Inspection of Accuracy

High conversion rate (conversion rate of monomer higher than 98%) and low conversion rate (conversion rate of monomer lower than 80%) samples of PAA system (A), PMAA system (B) and PMA system (C) were tested on repeatability and standard addition recovery (each sample was determined by repeting seven times). The results are shown in Tables 2 and 3. In high conversion rate samples, the concentration of monomers was relatively low (less than $0.050 \times 10^{-3}$ mol $L^{-1}$), relative standard deviation (RSD) was 3.1–8.7% and standard addition recovery rate was 91.5–102.8%. In samples of low conversion rate, the concentration of monomers was relatively high (more than $0.200 \times 10^{-3}$ mol $L^{-1}$), RSD was less than or close to 1%, and standard addition recovery rate was 96.3–103.1%. All results proved the good repeatability and accuracy of the method by which monomers in PCs copolymerization system were determined.

### Comparison with Bromine Addition Redox Titration Method

Comparing chromatographic determination with bromine addition redox titration (are shown in Tables 2, 3), it can be seen that the determination results were similar to each other. But RSD of chromatographic method was less than titration method, which indicated that the repeatability of this method was better. And also, because of pure sensitivity, it was difficult to determine low concentration monomers in high conversion rate system using the titration method. On the contrary, chromatographic method was significantly more sensitive than bromine addition redox titration method and might be a better method especially for high conversion rate samples.

## Conclusion

1. Seven kinds of residual monomers were quantitatively determined on a SinoChrom ODS-BP (C18) column and UV detector. The mobile phases which were used to determine micromolecular monomers composed of acetonitrile-phosphate buffer solution (0.05 mol $L^{-1}$, pH = 3) in the ratio of 8:92 (*v*/*v*). While the mobile phases of testing long side-chain monomers composed of acetonitrile-phosphate buffer solution (0.05 mol $L^{-1}$, pH = 6.5) in the ratio of 40:60 (*v*/*v*). The residual monomers were detected by UV detector at 205 nm.
2. The orders of magnitude of linear response amounted to three by chromatographic method. Under this condition, the detection limit of blank matrix with

**Table 1** Regression equations of the calibration curves, retention times and detection limits of the investigated compounds

| Monomer | Concentration range ($10^{-5}$ mol $L^{-1}$) | Regression equation | $r^2$ | Detection limit ($10^{-5}$ mol $L^{-1}$)[a] | Detection limit ($10^{-5}$ mol $L^{-1}$)[b] |
|---|---|---|---|---|---|
| AA | 0.20–200 | $Y = 744.5X + 2.1$ | 0.9994 | 0.014 | 0.24 |
| MAA | 0.20–200 | $Y = 744.5X + 2.1$ | 0.9996 | 0.013 | 0.16 |
| MA | 0.10–100 | $Y = 1{,}645.5X + 4.3$ | 0.9991 | 0.007 | 0.12 |
| MAS | 0.20–200 | $Y = 251.9X - 1.0$ | 0.9991 | 0.020 | 0.32 |
| AMPS | 0.20–200 | $Y = 1{,}295.8X - 2.5$ | 0.9996 | 0.009 | 0.16 |
| MPEGA | 0.40–200 | $Y = 757.7X + 0.8$ | 0.9992 | 0.08 | 0.6 |
| MPEGMA | 0.40–200 | $Y = 793.4X + 1.3$ | 0.9994 | 0.09 | 0.8 |

[a] By standard solution

[b] By spiked blank samples

**Table 2** The results of the analysis of high conversion samples

| | System (A) | | | System (B) | | | System (C) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Measured value ($10^{-3}$ mol kg$^{-1}$) | RSD (%) | Recovery (%)[a] | Measured value (mol kg$^{-1}$) | RSD (%) | Recovery (%)[a] | Measured value (mol kg$^{-1}$) | RSD (%) | Recovery (%)[a] |
| AA | 2.1 | 4.5 | 96.1 | – | – | – | – | – | – |
| MAA | – | – | – | 1.7 | 4.8 | 102.8 | – | – | – |
| MA | – | – | – | – | – | – | 3.9 | 3.1 | 102.8 |
| MAS | 4.8 | 3.4 | 91.5 | 4.4 | 5.2 | 92.7 | 4.5 | 4.7 | 94.6 |
| AMPS | 3.0 | 3.2 | 99.4 | – | – | – | 1.7 | 5.2 | 97.4 |
| MPEGA | 1.8 | 8.7 | 98.7 | – | – | – | 2.4 | 6.8 | 99.3 |
| MPEGMA | – | – | – | 2.8 | 6.3 | 93.5 | – | – | – |
| Total | 11.7 | 2.2 | – | 8.9 | 3.4 | – | 12.5 | 2.4 | – |
| Total (by titration) | 12.5 | 5.6 | – | 9.4 | 8.2 | – | 12.8 | 5.7 | – |

[a] Standard addition was $2.00 \times 10^{-3}$ mol kg$^{-1}$

**Table 3** The results of the analysis of low conversion samples

| | System (A) | | | System (B) | | | System (C) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Measured value ($10^{-3}$mol kg$^{-1}$) | RSD (%) | Recovery (%)[a] | Measured value ($10^{-3}$ mol kg$^{-1}$) | RSD (%) | Recovery (%)[a] | Measured value ($10^{-3}$ mol kg$^{-1}$) | RSD (%) | Recovery (%)[a] |
| AA | 51.4 | 0.43 | 102.5 | – | – | – | – | – | – |
| MAA | – | – | – | 151.2 | 0.56 | 96.3 | – | – | – |
| MA | – | – | – | – | – | – | 43.9 | 0.48 | 98.8 |
| MAS | 45.7 | 1.0 | 101.7 | 116.8 | 0.78 | 97.6 | 124.8 | 0.64 | 105.2 |
| AMPS | 21.8 | 0.55 | 98.4 | – | – | – | 25.9 | 0.51 | 97.3 |
| MPEGA | 27.9 | 1.1 | 99.6 | – | – | – | 33.4 | 0.57 | 101.6 |
| MPEGMA | – | – | – | 27.1 | 0.89 | 103.1 | – | – | – |
| Total | 146.8 | 0.41 | – | 295.1 | 0.43 | – | 228.0 | 0.38 | – |
| Total (by titration) | 143.4 | 0.67 | – | 298.2 | 0.65 | – | 221.9 | 0.54 | – |

[a] Standard addition was $20.0 \times 10^{-3}$ mol kg$^{-1}$

additional standard solution was $0.12 \times 10^{-5}$–$0.8 \times 10^{-5}$ mol L$^{-1}$. Determination results of high and low conversion rate samples were proved to have good repeatability and accuracy.

**Acknowledgments** The authors gratefully acknowledge the Western Region Traffic Construction Technology Program of the Ministry of Communications of China (No. 2007319811130).

## References

1. Rößler C, Eberhardt A, Kučerová H, Möser B (2008) Influence of hydration on the fluidity of normal Portland cement pastes. Cem Concr Res 38(7):897–906. doi:10.1016/j.cemconres.2008.03.003
2. Hommer H (2009) Interaction of polycarboxylate ether with silica fume. J Eur Ceram Soc 29(10):1847–1853. doi:10.1016/j.jeurceramsoc.2008.12.017
3. Plank J, Hirsch C (2007) Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. Cem Concr Res 37(4):537–542. doi:10.1016/j.cemconres.2007.01.007
4. Plank J, Winter Ch (2008) Competitive adsorption between superplasticizer and retarder molecules on mineral binder surface. Cem Concr Res 38(5):599–605. doi:10.1016/j.cemconres.2007.12.003
5. Zhang R, Guo H, Lei J, Zhang A, Gu H (2007) Effect of molecular structure on the performance of polyacrylic acid superplasticizer. J Wuhan Univ Technol 22(2):245–249. doi:10.1007/s11595-006-2245-9
6. Zhang R, Li Q, Zhang A, Liu Y, Lei J (2008) The synthesis technique of polyacrylic acid superplasticizer. J Wuhan Univ Technol 23(6):830–833. doi:10.1007/s11595-008-6830-y
7. Yamada K, Takahashi T, Hanehara S, Matsuhisa M (2000) Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer. Cem Concr Res 30(2):197–207. doi:10.1016/S0008-8846(99)00230-6
8. Houst YF, Bowen P, Perche F, Kauppi A, Borget P, Galmiche L, Le Meins J-F, Lafuma F, Flatt RJ, Schober I, Banfill PFG, Swift DS, Myrvold BO, Petersen BG, Reknes K (2008) Design and function of novel superplasticizers for more durable high

performance concrete (superplast project). Cem Concr Res 38:1197–1209. doi:10.1016/j.cemconres.2008.04.007
9. Giraudeau C, d'Espinose de Lacaillerie J-B, Souguir Z (2009) Surface and intercalation chemistry of polycarboxylate copolymers in cementitious systems. J Am Ceram Soc 92(11): 2471–2488. doi:10.1111/j.1551-2916.2009.03413.x
10. Li Chongzhi (2004) Study on the synthesis and properties of novel polycarboxylate-type high range water-reducers. Dissertation for the degree of Doctor of Engineering. Tsinghua University, China. doi:CNKI:CDMD:1.2005.035287 (http://dlib.edu.cnki.net/kns50/detail.aspx?dbname=CDFD2005&filename=2005035287.nh)
11. Jamshidi A, Ahmad Khan Beigi F, Kabiri K, Zohuriaan-Mehr MJ (2005) Optimized HPLC determination of residual monomer in hygienic SAP hydrogels. Polym Test 24(7):825–828. doi: 10.1016/j.polymertesting.2005.07.007
12. Urban VM, Cass QB, Oliveira RV, Giampaolo ET, Machado AL (2006) Development and application of methods for determination of residual monomer in dental acrylic resins using high performance liquid chromatography. Biomed Chromatogr 20(4):369–376. doi:10.1002/bmc.575
13. Viljanena EK, Langerb S, Skrifvarsc M, Vallittu PK (2006) Analysis of residual monomers in dendritic methacrylate copolymers and composites by HPLC and headspace-GC/MS. Dent Mater 22:845–851. doi:10.1016/j.dental.2005.11.012
14. Feng L, Gao Z, Bian X, Chen Z, Chena X, Chen W (2009) A quantitative HPLC method for determining lactide content using hydrolytic kinetics. Polym Test 28:592–598. doi:10.1016/j.polymertesting.2009.04.005
15. Chai XS, Houa QX, Schork FJ (2004) Determination of residual monomer in polymer latex by full evaporation headspace gas chromatography. J Chromatogr A 1040:163–167. doi:10.1016/j.chroma.2004.04.024
16. Sakai E, Yamada K, Ohta A (2003) Molecular structure and dispersion-adsorption mechanisms of Comb-type superplasticizers used in Japan. J Adv Concr Technol 1(1):16–25. doi:10.3151/jact.1.16
17. Wu H, Guo H, Lei J, Zhang R, Liu Y (2007) Research on synthesis and action mechanism of polycarboxylate superplasticizer. Front Chem China 2(3):322–325. doi:10.1007/s11458-007-0060-2
18. Berthod A, Tomer S, Dorsey JG (2001) Polyoxyethylene alkyl ether nonionic surfactants: physicochemical properties and use for cholesterol determination in food. Talanta 55:69–83. doi: 10.1016/S0039-9140(01)00395-2