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Characterization of polyethylene glycols and polypropylene glycols by capillary zone electrophoresis and micellar electrokinetic chromatography

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Abstract

Methods based on capillary zone electrophoresis (CZE) and micellar electrokinetic chromatography (MEKC) have been developed and optimized for the separation of polyethylene glycols (PEGs) and polypropylene glycols (PPGs). To provide for charge and detectability both types of polymeric compounds were derivatized with phthalic anhydride (PhAH) or 1,2,4-benzenetricarboxylic anhydride (BTA) before the separation. Derivatization with BTA yielded more complex electropherograms, due to the occurrence of different isomeric reaction products for every PEG or PPG species. Effective mobilities of the PhAH derivatives were related to the number of monomer units in the polymers in a straightforward way. The CZE method could also be used to determine the monomer-number distribution of random and block PEG–PPG copolymers. For an MEKC analysis the PEGs and PPGs were derivatized with phenyl isocyanate. Oligomers of PEGs could be separated up to molecular masses of 5000, while for the more hydrophobic PPGs oligomeric separation was only accomplished for molecular masses of up to 1500. Due to a strongly different separation mechanism for the PEG and PPG derivatives in the MEKC system, a complete group separation of the two types of polymer molecules could be obtained.
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1. Introduction

Linear polyethylene glycols (PEGs) and the more hydrophobic polypropylene glycols (PPGs) are important classes of synthetic polymers. PEGs are nontoxic water-soluble compounds that are widely employed as intermediates for the manufacture of nonionic surfactants and as additives in pharmaceutical ointments, cosmetic creams and lotions. PPGs can be applied as plasticizers or lubricants. However, their main use is as intermediates in the production of polyurethane [1].

Characterization of PEGs and PPGs is an important issue in controlling manufacturing processes and for the identification of additives in commercial products. Characteristics to be determined are the chemical (monomer) composition of the polymeric compounds, end-group functionalities, the average molecular mass (M_r) and the molecular mass distribution (MMD). Details on the chemical structure and end-groups of PEG and PPG (co-)polymers can be obtained by normal-phase or reversed-phase high-performance liquid chromatography (NP- or RP-HPLC) [2], by supercritical-fluid chromatography

(SFC) [3] or by matrix-assisted laser-desorption/ ionisation time-of-flight mass spectrometry (MALDI–TOF-MS) [4]. By MALDI–TOF-MS the molecular mass for each species of polydisperse samples of PEGs or PPGs can be obtained exactly. However, for MMD determinations MALDI–TOF-MS is less suitable, since at a relative high polydispersity errors can occur in quantification due to different sensitivities for shorter and longer polymer chains. For the characterization of the MMD of PEGs and PPGs size-exclusion chromatography (SEC) is by far the most commonly applied technique, often combined with viscosity and/or light-scattering detection techniques [5].

Capillary zone electrophoresis (CZE) has demonstrated its value as a rapid, highly efficiency tool for the analysis of a variety of compounds, including inorganic ions, small molecules and (bio)macromolecules [6]. It has been shown that the CZE principle is relevant for the determination of the MMD of synthetic polymers [7,8]. Both Bullock [9] and Vanhoenacker et al. [10] demonstrated CZE analyses of PEGs after their derivatization with phthalic anhydride (PhAH). At a pH of 9, the double derivatized PEGs have a charge of -2 and migrate against the electroosmotic flow (EOF), with the largest polymeric compounds eluting first. PEG samples could be separated into their individual oligomers up to a molecular mass of 3000 [9]. It was possible to separate higher-molecular-mass PEGs by using a sieving matrix. Wallingford [11] reported capillary gel electrophoresis (CGE) of PEGs with molecular masses of up to 5000. The end groups of the PEGs were also derivatized with PhAH. The main disadvantage of this operating system was the long analysis time; more than 1.5 h were needed for the separation of a sample of PEG 4600. Higher effective mobilities and an improved efficiency were reported by Barry et al. [12], who used 1,2,4-benzenetricarboxylic anhydride (BTA) as a derivatization reagent. PEG derivatives with a charge of -4 were separated into their individual oligomers until molecular masses up to 5000, but with shorter analysis times than the earlier mentioned CGE method.

Recently, CZE separations of PEGs after derivatization with monodisperse DNA strands have been shown [13]. In this mode, the charged DNA polymer is thought of as an "electrophoretic engine" and the PEG chains coupled to them are regarded as an "electrophoretic parachute". The report showed oligomer resolution for PEGs with molecular masses up to 5000.

The separation of neutral (polymeric) compounds can be achieved by micellar electrokinetic chromatography (MEKC). High organic solvent content in the buffer, often necessary for the solubility of the compounds, breaks down the micelle structures. However, it has been demonstrated that smaller aggregates of the surfactants are still present in solution, which still results in interaction between analytes and the surfactants [14]. Jorgenson and Walbroehl [15] have described this mechanism as solvophobic association. Efficient MEKC separations of alkylphenol polyethoxylates based on this solvophobic association mechanism have been described [9,16–19]. The reports show baseline separations of the compounds based on differences in the chain length of the PEG side-chain.

In the work reported here, fast and straightforward CZE and MEKC systems for the characterization of linear PEGs and PPGs are described and compared. Prior to CZE separation the hydroxyl end-groups were converted by reaction with PhAH or BTA and prior to MEKC separation a derivatization was carried out by reaction with phenyl isocyanate. CZE and MEKC separation mechanisms for the derivatized PEGs and PPGs are discussed and the quantitative accuracy of these two forms of electrophoresis is studied by comparing the results with MALDI–TOF-MS measurements.

2. Experimental

2.1. Chemicals

Samples of PEG 200, 400, 1000, 1500 and 4000 were obtained from Merck (Darmstadt, Germany). PEG 600, 2000, PPG 2000 and block co-polymers of ethylene oxide (EO) and propylene oxide (PO) came from Aldrich (Steinheim, Germany). PPG 400 and 1000 samples and a narrow PEG 600 standard were obtained from Polysciences (Eppelheim, Germany). The internal standard, pentaethylene glycol (E_5), was obtained from Fluka (Buchs, Switzerland) and the

PPG internal standard 1,2-propanediol came from Merck. Phthalic anhydride (British Drughouse), 1,2,4-benzenetricarboxylic anhydride (Aldrich) and phenyl isocyanate (Acros) were all used as derivatization reagents. Borate buffers were prepared by dissolving disodium tetraborate–decahydrate (Merck) in sub-boiled demi-water. All other chemicals used were of analytical-grade quality.

2.2. Apparatus

All experiments were performed using a Prince CE injection system (Prince Technologies, Emmen, The Netherlands) in combination with a variable-wavelength UV detector (Linear UVIS 200, Linear Instruments, Reno, NV, USA). Detection of the PhAH and BTA derivatives was performed at 220 nm, while the phenyl isocyanate derivatives were detected at 235 nm. Fused-silica capillaries, obtained from Composite Metal Services (The Chase, UK), of 50 μm I.D. with a total length of 58 cm and a detection window at 44 cm were used. New capillaries were flushed with 0.1 M HCl, 0.1 M NaOH and water for 5, 15 and 3 min, respectively. Before each series of experiments, the capillary was rinsed with 0.1 M NaOH, water and finally with the buffer solution. All samples were injected by a pressure of 20 mbar for 6 s. Voltages of 10–25 kV were applied. Separations were performed at ambient temperature. Data handling was carried out with WinPrince control software (Prince Technologies) and Dax data-acquisition and analysis software (Van Mierlo Software Consultancy, Eindhoven, The Netherlands).

The MALDI–TOF-MS instrument was a Bruker model Biflex (Bremen, Germany). The MALDI was equipped with a 337-nm UV laser and a high-resolution microchannel plate (MCP) detector in the reflection mode. Polymers (1 mg/ml) and the matrix ditranol (40 mg/ml) were dissolved in tetrahydrofuran (THF) and mixed in a ratio of 1:4 (v/v) before deposition. No salt was added and the dry-droplet method was used for deposition.

2.3. Derivatization methods

Schemes of the derivatization reactions are shown in Fig. 1. The applied reaction conditions, based on previously published research [9–12,20,21], are described in Table 1. Amounts of 0.1–0.2 g of polymer samples were dissolved in 1 ml of solvent and a 5-fold excess of derivatization reagent and the catalyst were added. In this work the catalyst dibutyltindilaurate was added to increase the reaction rate of between phenyl isocyanate and the hydroxyl
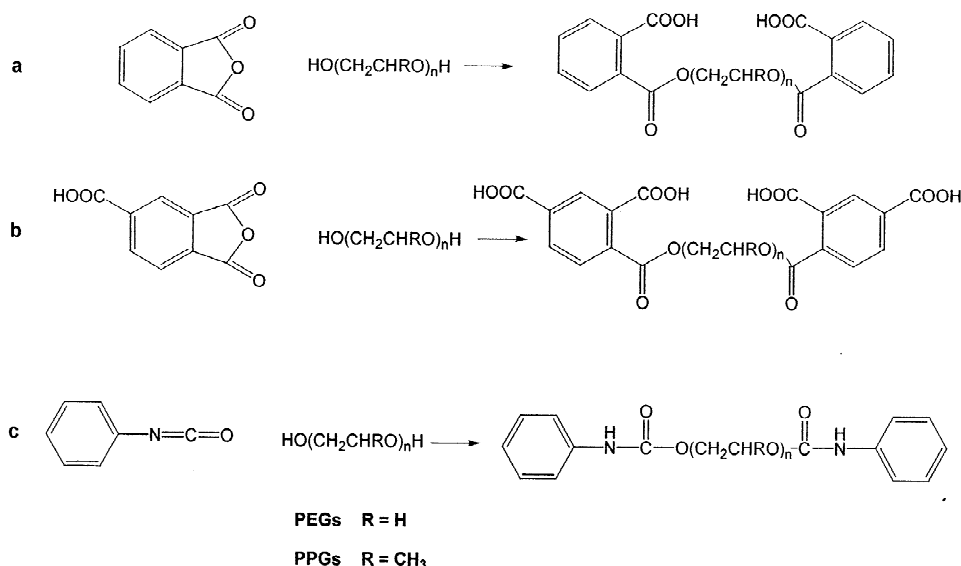

Fig. 1. Scheme of the derivatization reactions with (a) PhAH, (b) BTA and (c) phenyl isocyanate.

Table 1
Derivatization conditions

	CZE (PhAH)	CZE (BTA)	MEKC
Solvent	Pyridine	THF	Acetonitrile
Reagent	PhAH	BTA	Phenyl isoyanate
Catalyst	Imidazole (0.3 M)	–	Dibutyltindilaurate (10^{-5} M)
Temperature (°C)	95	95	55
Time (h)	16	16	2

groups of the polymers and to improve the number of double derivatized polymers. After homogenization, the solutions were placed in an oven at a temperature and for a period of time as given in Table 1. The derivatized samples were left to cool to room temperature and diluted 20–100 times with acetonitrile before injection.

2.4. Sample preparation

A 1-ml aliquot of a cosmetic solution (face lotion) was dried in a GC oven at 105 °C for 16 h. The dried residue was dissolved in 1 ml of acetonitrile. Derivatization by phenyl isocyanate was performed as described above. For identification of the peaks the internal standard was added to the sample.

3. Results and discussion

3.1. CZE of PEGs and PPGs derivatized with PhAH

It appeared that for an optimal CZE separation of the PhAH derivatized polymeric compounds, reduction of the EOF was necessary. The EOF can be reduced most conveniently by adding organic solvents to the separation buffer. Fig. 2 shows the separation of a derivatized PEG 600 sample with 30% acetonitrile, methanol or THF added to a borate buffer (25 mM disodium tetraborate). The EOF mobility was reduced to 36, 24 and 20·10^{-9} m^2 V^{-1} s^{-1}, respectively. Complete oligomeric baseline separation was achieved with all systems and no significant differences were apparent in peak shapes
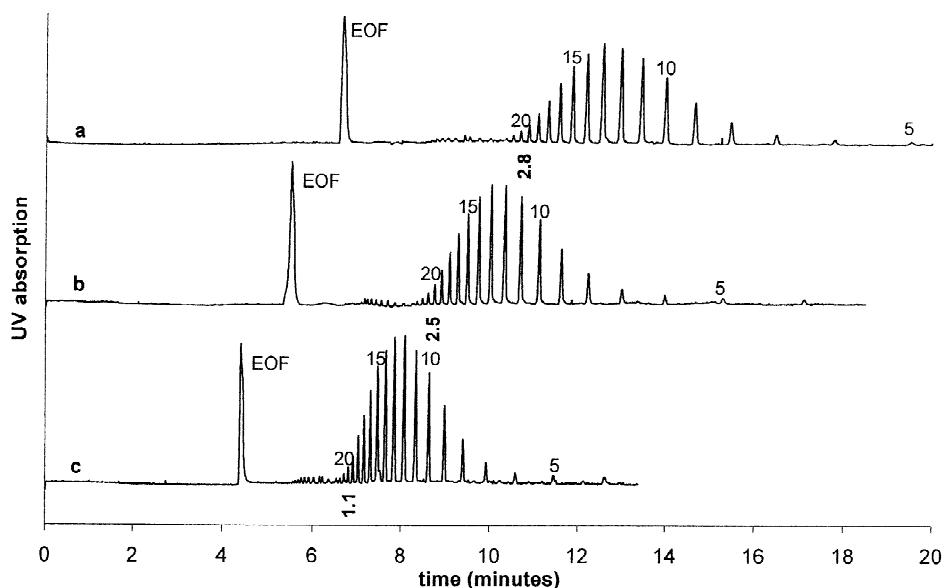

Fig. 2. CZE separation of PhAH derivatized PEG 600 with a borate buffer containing 30% (v/v) of (a) THF at 30 kV, (b) methanol at 30 kV or (c) acetonitrile at 25 kV. The resolution value for the peaks with monomer number 20 and 21 are indicated in the figure.

or selectivities. Plate numbers were in the order of 250 000. Resolution values of the PEG oligomers with chain lengths of 20 and 21 monomers are shown below the electropherograms. With the 30% acetonitrile separation buffer, complete oligomeric baseline separation of PEGs with chain lengths of up to 35 monomers ($M_r \sim 1500$) was achieved in 12 min. Previously published separations of equal molecular mass PEGs showed longer analysis times with more complicated buffer compositions [9,11]. A further reduction of the EOF velocity, by using methanol or THF as organic modifier, improved the resolution between higher oligomer peaks, at the expense of a longer analysis time. With 50% methanol an oligomeric characterization of PEGs with molecular masses of up to 4000 was possible. An electropherogram of the separation of a PEG 2000 sample in such a buffer is shown in Fig. 3. This work shows that linear PEGs with average molecular mass of up to 4000 could be characterized within short analysis times using straightforward buffer compositions. However, for the characterization of PEGs with still higher-molecular-masses the use of sieving matrices has been suggested [11,12].

Since the electrophoretic mobility of (end-labeled) charged compounds in CZE is proportional to their charge-to-friction ratio, and all PhAH derivatized polyethers have the same charge (-2), the reciprocal of the electrophoretic mobility ($1/\mu$) is expected to mainly reflect the effective size of the derivatized polymers. A plot of the reciprocal of the mobility versus the number of monomeric units (n) for PEGs is shown in Fig. 4. It was found that the inverse mobility increased almost perfectly linearly with n. Similar results have been reported for the free solution electrophoretic separation of PEG–DNA conjugates [13], DNA–protein complexes [22,23], oligosaccharides [24] and fatty acids [25]. The linear and highly repeatable behaviour made it possible to apply a one-point calibration, with E_5 as calibration point, for an unambiguous determination of the number of monomeric units for a specific peak.

The buffer composition used for the separation of low-M_r PEGs (30% acetonitrile in 25 mM borax) was also used for the separation of the more hydrophobic PPGs, of which both hydroxyl end-groups were also converted with PhAH prior to the separation. The effective mobilities, peak shapes and resolution of the PPGs were similar to those of PEGs with similar molecular mass. A plot of the inverse effective mobility versus the n for the investigated PPGs is depicted in Fig. 4. 1,2-Propanediol was used
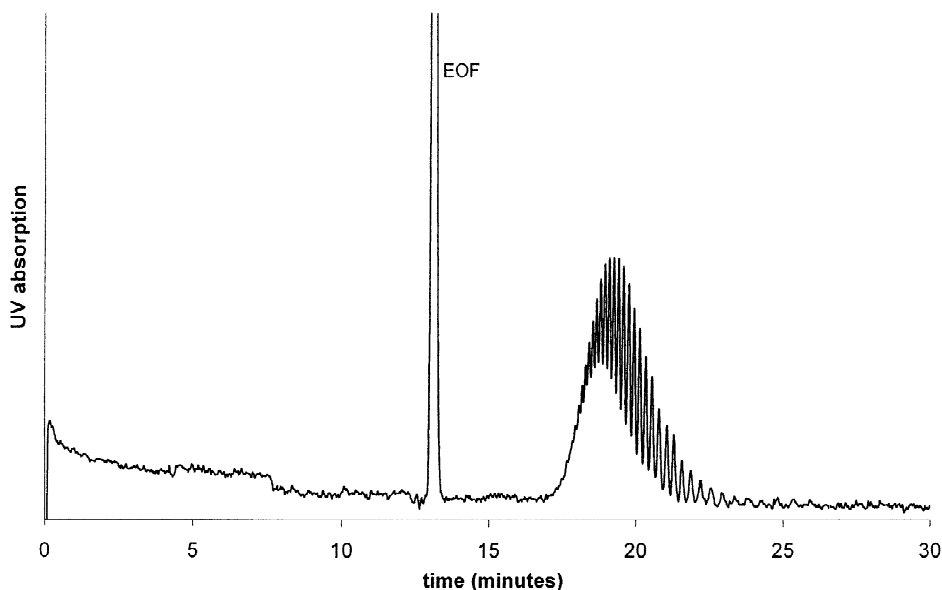

Fig. 3. CZE separation of PhAH derivatized PEG 2000 with a borate buffer containing 50% (v/v) of methanol at 25 kV.
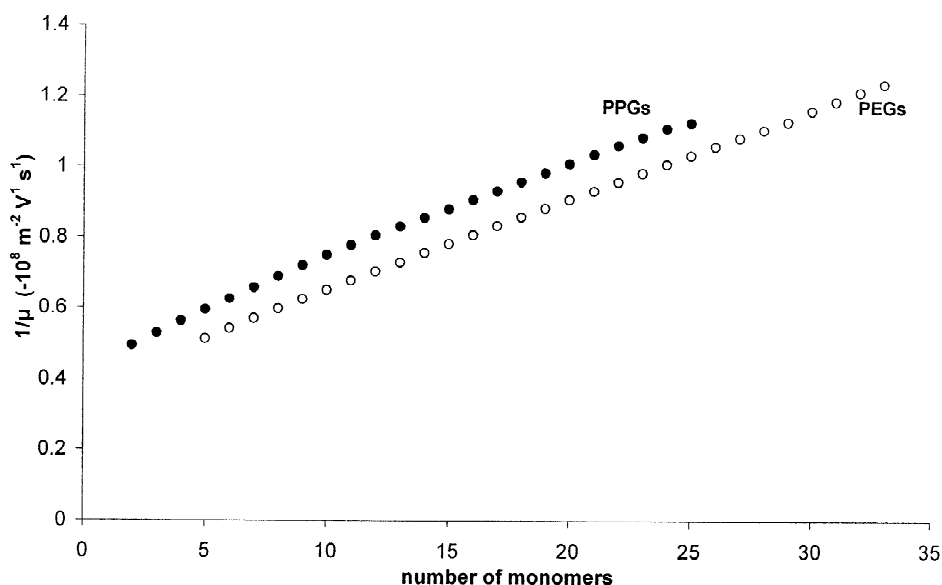
Fig. 4. Plots of the reciprocal of the electrophoretic mobilities of PhAH derivatized PEGs and PPGs as a function of the number of monomeric units. Buffer containing 30% (v/v) acetonitrile.

as a calibration point for the determination of the monomer number of the PPG peaks. It is shown that in this particular buffer system, the low-M_r PPGs are slightly more bulky than the corresponding PEGs (with the same n). At higher-molecular-mass values the plot of $1/\mu$ versus n for the PPGs is slightly curved. This may be the result of intramolecular interactions within longer PPG chains that may reduce their effective size in solution.

The separation of a mixture of PEGs and PPGs by CZE is not possible; the two polymeric compounds give two overlapping sets of peaks (Fig. 5). The observed difference in effective size of derivatized PEGs and PPGs depends on the composition of the separation buffer. In contrast to the findings using a 30% acetonitrile (ACN) solution (as in Fig. 4), in a buffer containing 50% (v/v) acetonitrile the mobilities of PEGs and PPGs with the same number of monomers are approximately equal. This provides an opportunity to determine the MMD of PEG–PPG co-polymers with hardly any influence of the EO/PO composition. Fig. 6 shows the monomer-number distribution, as constructed from the measured electropherogram, of a PEG–PPG block copolymer with a nominal M_r of 1100 and an average EO content of

10%. Despite the inherent variation in the number of EO and PO monomers in the individual chains, well-defined peaks are obtained for oligomer numbers exceeding 30. For this particular sample a peal molecular mass (M_p) of 1095 ($n = 19$), a weight-average molecular mass (M_w) of 1203 and a polydispersity (M_w/M_n, where M_n is the number-average mass) of 1.03 were found. Also, for a random PEG–PPG copolymer (nominal M_r 2500, 75% EO) individual peaks could be discerned up to a polymerization degree of 50.

3.2. CZE of PEGs derivatized with BTA

It has been argued that an increase in charge of the polymer species to be separated may result in improved efficiency [12] and may allow for oligomeric separation of longer polymer chain lengths. Derivatization of PEGs with BTA results in derivatives with a charge of -4 (Fig. 1). Fig. 7 shows the CZE separation of a PEG 600 sample derivatized with BTA, which was carried out in a borate buffer containing 30% THF. Since the hydroxyl groups of the PEGs can bind either at the *meta*- or the *para*-carboxy group of BTA (relative to the third car-
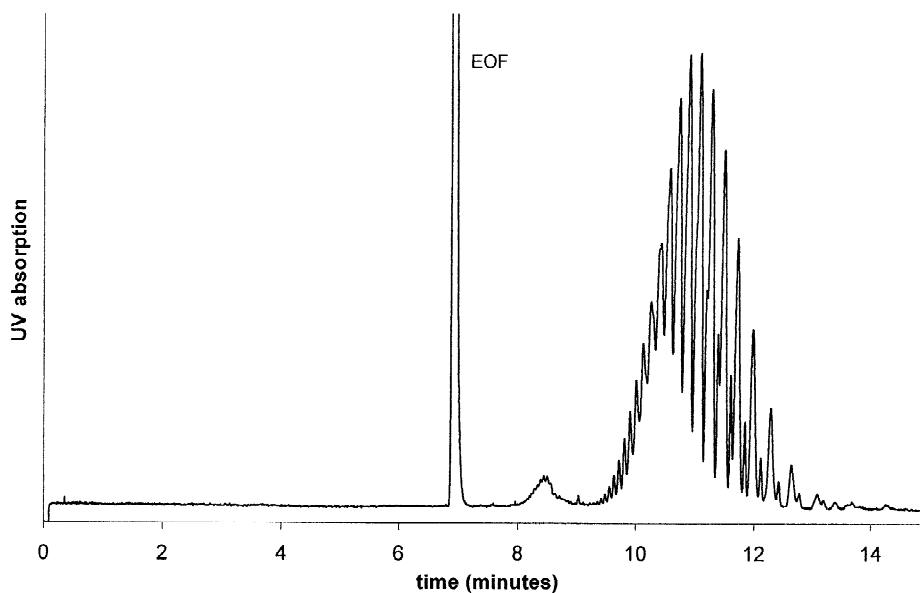
Fig. 5. CZE electropherogram of a mixture of (PhAH derivatized) PEG 1000 and PPG 1000. Borate buffer contained 30% methanol at a voltage of 25 kV.

boxylic acid group on the BTA molecule), two-sided derivatization of PEG oligomers with BTA resulted in three isomeric peaks for every monomer number.

The derivatization was (deliberately) incomplete. The electropherogram shows that for the single-sided derivatives two isomers were formed. Formation of
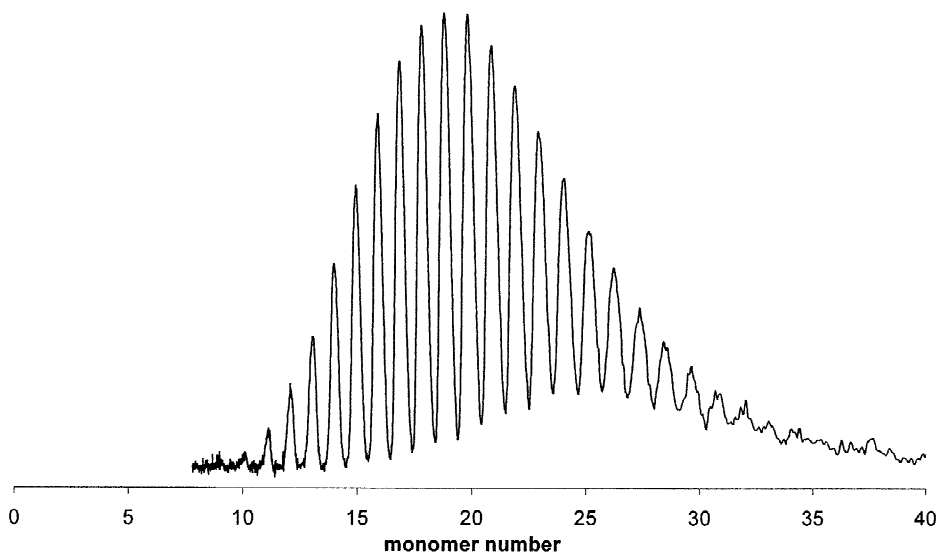

Fig. 6. Monomer-number distribution of a PEG–PPG block copolymer (10% PEG) as obtained from a CZE separation, with a borate buffer containing 50% (v/v) acetonitrile.
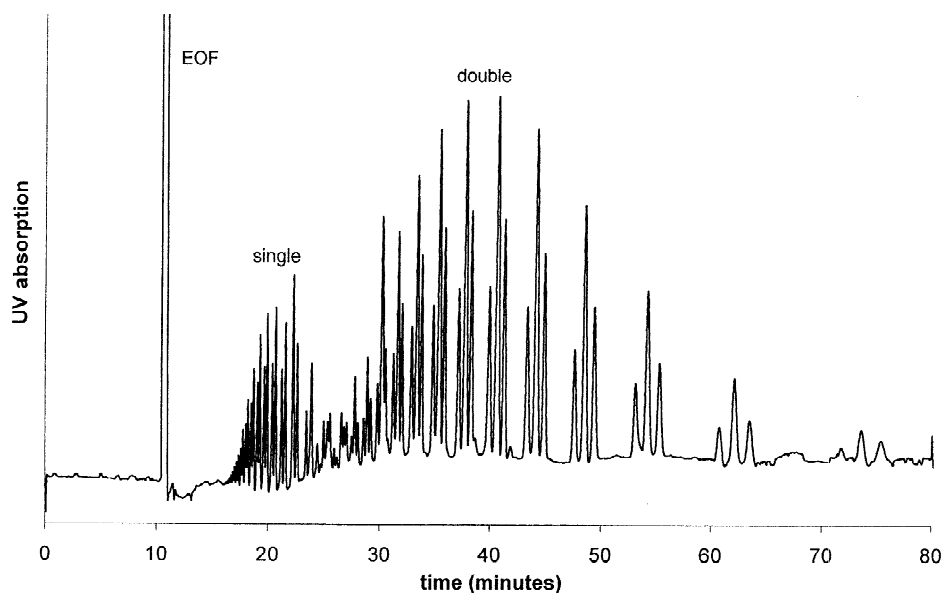
Fig. 7. CZE electropherogram of a PEG 600 sample (incompletely) derivatized with BTA. For conditions see text. Voltage 25 kV.

isomers was not reported by Barry et al. [12], although in their CGE electropherogram of a sample of octylphenol ethoxylate some peak splitting can be observed. Because of the increased complexity of the electropherograms, we found that derivatization with BTA showed no improvement compared with the PhAH method.

3.3. MEKC of PEGs and PPGs

In a mixed sample PEGs and PPGs of equal molecular masses cannot be identified separately by CZE. Since PEGs and PPGs differ in their polarity, separation of these two compounds can be based on this property. It has been reported previously that different alkylphenol polyethoxylates (PEG surfactants) were separated by interaction with sodium dodecyl sulfate (SDS) aggregates in an MEKC system [9,16–18]. In our work, the hydroxyl end-groups of linear bare PEGs and PPGs were converted into hydrophobic UV-active tags by phenyl isocyanate. Conversion of the hydroxyl end-groups was achieved by adding the catalyst dibutyltindilaurate and heating the solution for at least 2 h. The completeness of the derivatization reaction was tested by MALDI–TOF-MS. In all MS spectra

recorded only doubly derivatized polymer chains were detected.

As in the CZE system, the experimental conditions in the MEKC system could be optimized for a specific M_r range of the PEG or PPG polymers. The degree of interaction between derivatives and SDS aggregates could be controlled by varying the concentration of SDS or the organic-modifier content of the separation buffer. PEG oligomers with molecular masses of up to 1000 could be baseline separated using a buffer solution of 20 mM borax, 50 mM SDS and 20% (v/v) THF. Plate numbers were in the order of 200 000.

Low-M_r PEGs are often applied as detergents in cosmetic products. After a simple preliminary clean-up, a sample of aqueous face lotion was analysed by the MEKC method optimized for low-M_r PEGs. Peak identification was performed with E_5, which had been added to the sample as internal standard (Fig. 8). The lotion sample contained PEGs with chain lengths between $n = 8$ and 21, and values for M_n and M_w of 621 and 646 were found, with a polydispersity (M_w/M_n) of 1.04.

Separation of PEGs with longer chain lengths required a stronger interaction between derivatives and aggregates, which was accomplished by increas-
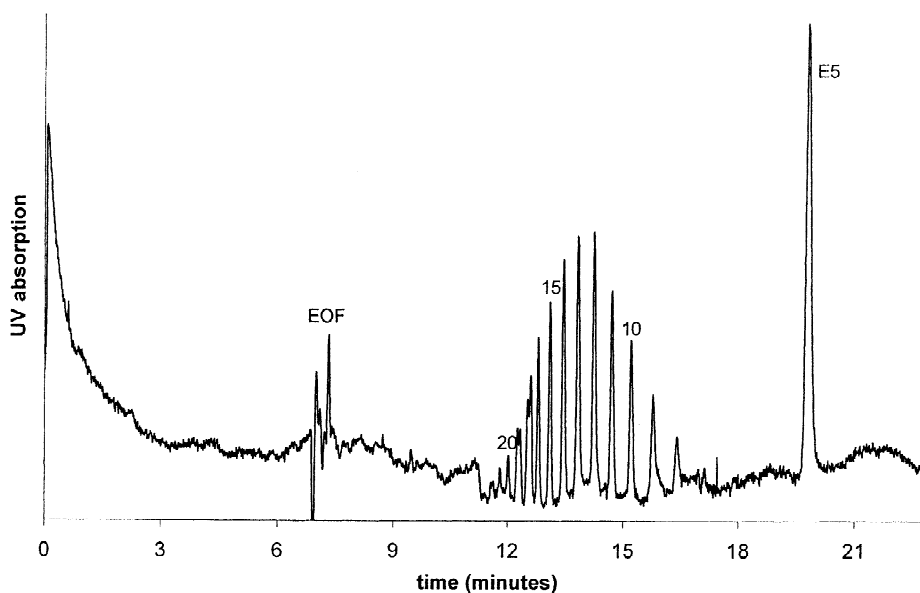
Fig. 8. MEKC analysis of a cosmetic product containing PEG. Conditions: 20 mM borax, 50 mM SDS and 20% THF. Voltage 25 kV.

ing the SDS concentration to 80 mM and decreasing the percentage THF to 10% (v/v). Under these conditions complete oligomeric separation of PEGs with molecular masses of up to 5000 could be realized (Fig. 9). This upper molecular mass limit for

MEKC is somewhat higher than that obtained with the CZE method.

Plots of the reciprocal of the electrophoretic mobilities of the PEG derivatives against the number of monomeric units resulted in approximately
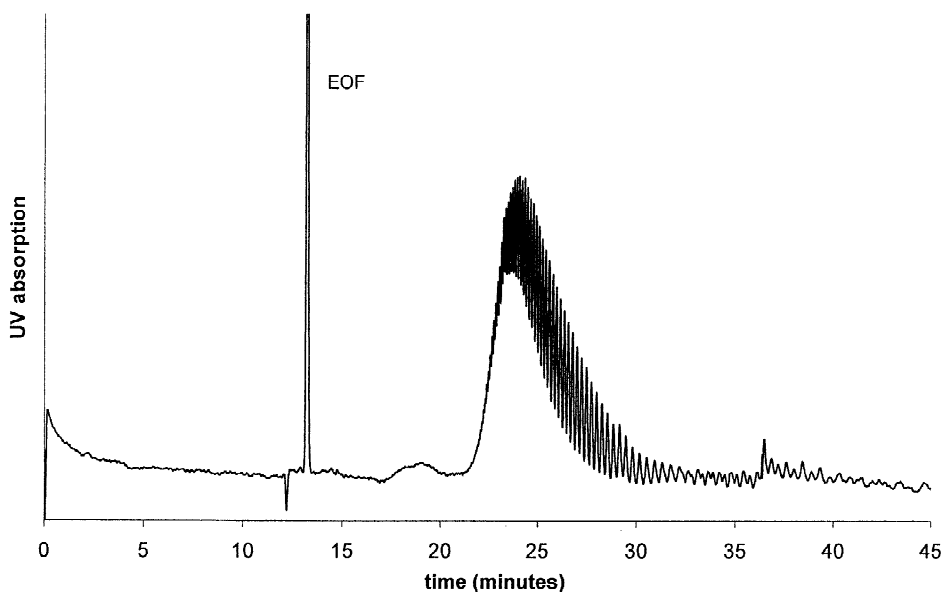

Fig. 9. MEKC separation of PEG 4000 after derivatization with phenyl isocyanate. Conditions: 20 mM borax, 80 mM SDS and 10% THF. Voltage 15 kV.
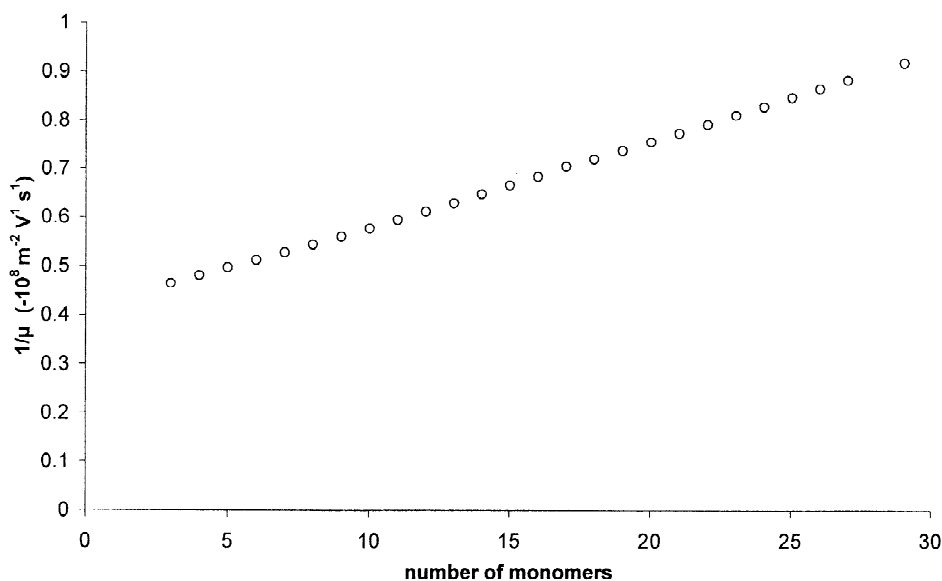
Fig. 10. Plot of the reciprocal of the apparent mobility in an MEKC system of phenyl isocyanate derivatized PEGs as a function of the monomer number.

straight lines (Fig. 10). This indicates that the derivatized end groups form aggregates with a more-or-less constant composition (charge) with SDS ions from the solution, while the length of the PEG chains determines the size of these aggregates.

The behaviour of the PPG derivatives in the MEKC system is completely different from that of the PEGs. Firstly, the hydrophobic PPGs interact more strongly with SDS aggregates. To favour the distribution between the pseudo stationary phase and the aqueous phase towards the latter, a higher percentage of organic modifier had to be added. By using acetonitrile as organic modifier the best separations and peak shapes were obtained. Still, the separation efficiency was lower than for the PEGs. With a buffer composition of 5 mM borax, 80 mM SDS and 30% (v/v) acetonitrile, a separation of PPGs derivatives with chain lengths of up to 25 monomers (M_r 1500) was achieved (Fig. 11). Secondly, from the electropherograms it can be seen that the effective mobilities of the PPG derivatives increase with the length of the polymer chain, while for the PEGs the mobilities decreased. These results suggest different separation mechanisms for phenyl isocyanate derivatives of PEGs and PPGs. Unlike for

PEGs (Fig. 9), for PPGs size is not the parameter that determines the mobility. Apparently, not only the derivatized end groups, but also the PPG chains interact with SDS.

In a real MEKC system, a linear relation between the value of $\log k'$ and the size of molecules in a homologue series is expected. Using Sudan Y as a marker for the micellar mobility, the peak times observed for the PPG peaks were converted to k' values, quantifying the distribution of the compounds between the micellar and the aqueous phase. In Fig. 12 an increase of the calculated $\log k'$ values with the number of monomers in the PPG derivatives is seen. However, the relation is far from linear, so that a simple MEKC-distribution model is insufficient to explain the behaviour of the PPG derivatives. It may be concluded that migrating PPG–SDS aggregates exist in solution, and that both the size and the charge of these aggregates vary significantly with the number of PO monomers in the polymer chains.

Because of the different behaviour of the PEG and PPG derivatives in an SDS solution, it was possible to separate a sample containing both polymeric compounds with similar molecular masses. An electropherogram obtained for a mixture of PEG 400 and
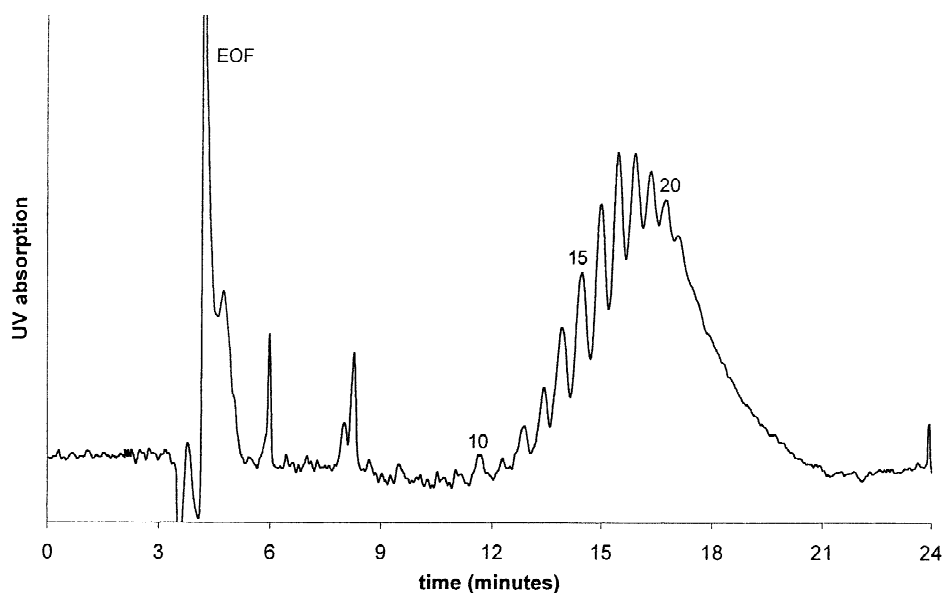
Fig. 11. MEKC separation of PPG 1000 after derivatization with phenyl isocyanate. For conditions see text. Voltage 25 kV.

PPG 400 is shown in Fig. 13. The separation was carried out using the conditions optimized for the separation of PPGs and therefore the separation of the PEG oligomers was not optimal. Two sets of peaks are observed, with a peak from the excess of reagent in between. A possible application of the MEKC method can be in the determination of the composition (distribution) of PEG–PPG co-poly-
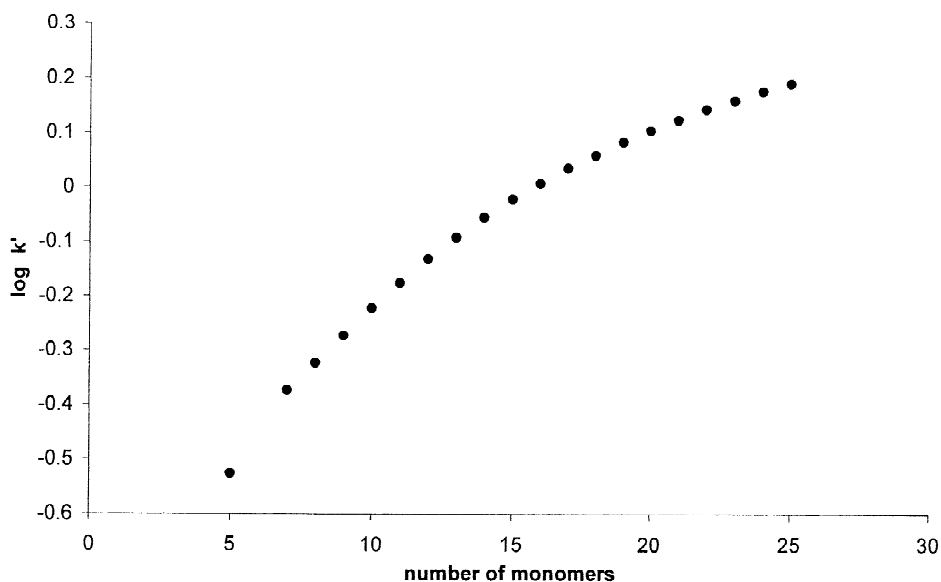

Fig. 12. Plot of log k' calculated from an MEKC separation of phenyl isocyanate derivatized PPGs as a function of the monomer number.
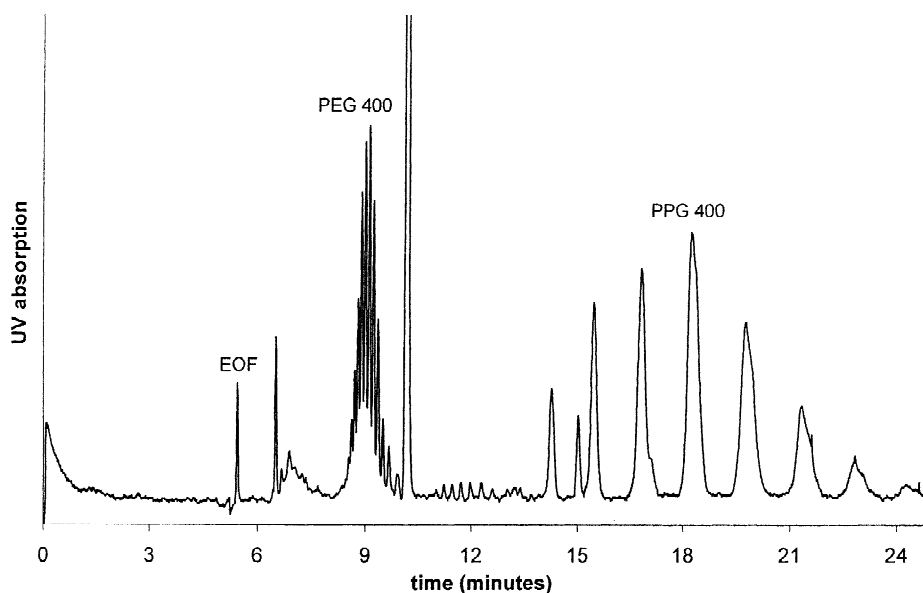
Fig. 13. MEKC separation of a mixture of PEG 400 and PPG 400. Conditions: 5 mM borax, 80 mM SDS and 30% acetonitrile. Voltage 25 kV.

mers. This aspect is presently the subject of further study.

3.4. Quantitative comparison

To validate the accuracy of the methods developed for the determination of the MMD of PEG and PPG polymers, a certified PEG 600 standard was analysed using optimized CZE and MEKC systems, and the results of these measurements were compared with MALDI–TOF-MS data and with the certificate of analysis of the standard. The M_p, M_w and M_w/M_n of the sample, as found with the different methods, are given in Table 2. In addition, the number of mono-mers corresponding to M_p and the range of monomer numbers of the detected peaks are given. CZE, MEKC and MALDI–TOF-MS can establish M_p at

the exact number of monomers, while the M_p value given in the certificate of analysis does not corre-spond to a molecular mass of a specific PEG oligomer. The spreading in the values of M_p mea-sured with CZE, MEKC and MS was only one monomer unit; with all methods M_p was lower than the value given in the certificate of analysis. With MALDI–TOF-MS a higher value for M_w was found than with the CE methods. Compounds with mono-mer numbers between 2 and 6 were not detected with MS. A possible explanation for this is that these compounds may evaporate due to the high vacuum before the actual measurement. The polydispersities as determined by CZE and MEKC were close to the value given in the certificate of analysis.

4. Conclusions

Characterization of linear PEGs and PPGs can be performed in a fast and efficient way by CZE after derivatization with PhAH. Oligomeric baseline sepa-ration was achieved for both types of polymeric compounds with average molecular masses of up to 2000. An approximately linear relationship of the inverse effective mobility versus the monomer num-

Table 2
Validation results for a PEG 600 standard

Method	Range of n	M_p (n)	M_w	M_w/M_n
CZE	2–23	546 (12)	605	1.06
MEKC	4–24	590 (13)	623	1.05
MALDI–TOF-MS	9–23	590 (13)	652	1.04
Certificate of analysis	–	620 (–)	–	1.05

ber was found, which makes peak identification straightforward with the use of a one-point calibration standard such as pentaethylene glycol or 1,2-propanediol. Above M_r 2000 the polymer samples were detected as a broad peak, but the determination of the average molecular mass and the polydispersity was still possible for compounds with molecular masses of up to 4000.

Mixtures of PEG and PPG polymers yielded electropherograms with overlapping sets of peaks. However, under suitable conditions the CZE method can be used to determine the monomer-number distribution of samples of (block or random) PEG–PPG copolymers.

Derivatization of the polyethers with 1,2,4-benzenetricarboxylic anhydride (BTA) yielded three isomers for each species, which complicated the resulting electropherograms. For practical application the derivatization with PhAH is therefore preferred.

The MEKC method allowed for the baseline separation of higher-M_r (up to 5000) PEG oligomers. Different separation mechanisms for PEGs and PPGs were observed. The MEKC method can be used for the characterization of samples containing a mixture of both polymeric compounds, giving two completely separated sets of peaks for the oligomers of the two types of polymers.

Assessment of the average molecular mass data and the polydispersity of a PEG 600 standard by CZE and MEKC showed results that were comparable with the certificate of analysis, better than the results of MALDI–TOF-MS.

Acknowledgements

References

[1] F.E. Baily, J.V. Koleske (Eds.), in: Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., Vol. A 21, 1992, pp. 579–589.

[2] K. Rissler, J. Chromatogr. 742 (1996) 1.

[3] B. Trathnigg, B. Maier, G. Schul, R.P. Kruger, U. Just, Macromol. Symp. 110 (1996) 231.

[4] N.H. Völcker, D. Klee, M. Hanna, H. Höcker, J.J. Bou, A.M. de Ilarduya, S. Muñoz-Guerra, Macromol. Chem. Phys. 200 (1999) 1363.

[5] H.G. Barth, B.E. Boyes, C. Jackson, Anal. Chem. 70 (1998) 251R.

[6] W.Th. Kok, Chromatographia 51 (2000) S1.

[7] W.Th. Kok, R. Stol, R. Tijssen, Anal. Chem. 72 (2000) 468A.

[8] H. Engelhardt, O. Grosche, Adv. Polym. Sci. 150 (2000) 189.

[9] J. Bullock, J. Chromatogr. 645 (1993) 169.

[10] G. Vanhoenacker, D. De Keukeleire, P. Sandra, J. Sep. Sci. 24 (2001) 651.

[11] R.A. Wallingford, Anal. Chem. 68 (1996) 2541.

[12] J.P. Barry, D.R. Radtke, W.J. Carton, R.T. Anselmo, J.V. Evans, J. Chromatogr. A 800 (1998) 13.

[13] W.N. Vreeland, C. Desruisseaux, A.E. Karger, G. Drouin, G.W. Slater, A.E. Barron, Anal. Chem. 73 (2001) 1795.

[14] R.M. Seifar, J.C. Kraak, W.Th. Kok, Anal. Chem. 69 (1997) 2772.

[15] J.W. Jorgenson, Y. Walbroehl, Anal. Chem. 58 (1986) 479.

[16] K. Heinig, C. Vogt, G. Werner, J. Chromatogr. A 745 (1996) 281.

[17] K. Heinig, C. Vogt, G. Werner, Fresenius J. Anal. Chem. 357 (1997) 695.

[18] C. Vogt, K. Heinig, Tenside Surf. Det. 35 (1998) 470.

[19] J.M. Herrero-Martínez, M. Fernández-Martí, E. Simó-Alfonso, G. Ramis-Ramos, Electrophoresis 22 (2001) 526.

[20] B. Björkqvist, H. Toivonen, J. Chromatogr. 153 (1978) 265.

[21] S.L. Wellons, M.A. Carey, D.K. Elder, Anal. Chem. 52 (1980) 1374.

[22] P. Mayer, G.W. Slater, G. Drouin, Anal. Chem. 66 (1994) 1777.

[23] C. Desruisseaux, D. Long, G. Drouin, G.W. Slater, Macromolecules 34 (2001) 44.

[24] J. Sudor, M.V. Novotny, Anal. Chem. 67 (1995) 4205.

[25] H. Cottet, P. Gareil, Electrophoresis 21 (2000) 1493.