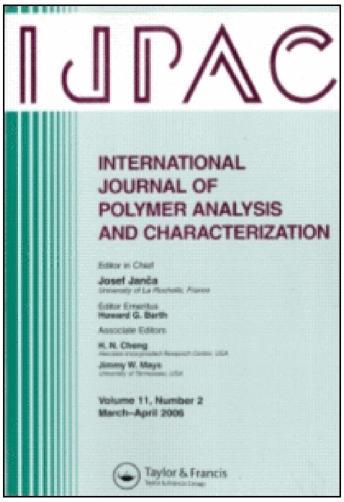

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Capillary Electrophoretic Analysis of Synthetic Copolymers with Indirect UV Detection and Contactless Conductivity Detection

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Abstract: Methods for the determination of non-UV-absorbing charged copolymers and polyelectrolytes by capillary electrophoresis with indirect UV detection (IUV) and contactless conductivity detection (CCD) were developed. Synthetic poly(ethylene glycol)-poly(methacrylic acid) copolymers (PEG-MAA) with different charge densities were separated in an arginine/sorbate buffer by free solution capillary electrophoresis. Blends of PEG-MAA copolymers and a high molar mass poly(methacrylic acid) sodium salt standard PMAA75k ($M_w = 75\,kg/mol$) have been separated, and the effect of the charge density on the detector signals has been investigated. The new experimental protocol enables the simultaneous recording of the CCD and the IUV signal in one single run. The arginine/sorbate buffer provides sufficient signal-to-noise ratios for indirect UV detection and contactless conductivity detection.

Keywords: Capillary electrophoresis; Contactless conductivity detection; Indirect UV detection; Methacrylic acid copolymers; Synthetic polyelectrolytes

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INTRODUCTION

Synthetic polyelectrolytes are used in many industrial applications, for example, as thickeners, dispersants, or flocculating agents. Polyelectrolyte copolymers like poly(ethylene glycol)-poly(methacrylic acid) (PEG-MAA) are used as modifiers in ready-made concrete to improve the flow properties. The effect of these additives, called superplasticizers, is linked to a tailoring of the interparticulate forces between the different concrete components.[1,2] To enhance the performance of such copolymers it is necessary to acquire knowledge about the copolymer composition, charge density, by-products, and impurities. Unfortunately, one encounters a number of problems when analyzing such samples by standard high-performance liquid chromatography (HPLC) methods. Because of the charged moieties, there are undesirable ionic or hydrophobic interactions with the stationary phase that make the chromatographic behavior of such samples unpredictable.

To avoid these problems, capillary electrophoresis (CE) appears to be a good choice. CE is a well-known analytical technique for the separation of inorganic and organic cations, anions,[3,4] and biological macromolecules.[3,5–9] In CE, the separation takes place according to the different electrophoretic mobilities μ of the analytes, which is a consequence of the different charge-to-radius ratios. In the past decade, an increasing number of studies have shown that CE is also a powerful analytical technique for the separation of synthetic polyelectrolytes.[10–27] But until now, only a few CE experiments on synthetic copolymers have been presented. Cottet and coworkers and Bohrisch and coworkers demonstrated that it is possible to separate polyelectrolyte copolymers according to their charge densities.[28–30] The different CE techniques and a number of applications have been dealt with in several recent review articles.[23,24,31,32]

Most of these experiments were carried out with UV-absorbing analytes because commercially available CE instruments are usually equipped with optical detection systems like UV or fluorescence detectors. This limits the application of capillary electrophoresis to UV-absorbing analytes. Unfortunately, the PEG-MAA copolymers do not exhibit sufficient absorbance to be detected by UV absorption at low concentration levels. To overcome this detection problem, indirect UV detection (IUV)[33–37] and conductivity detection can be used as alternative detection methods for non-UV-absorbing analytes. Indirect UV detection was first applied in CE by Hjertén et al.[33] and has since then been used successfully to analyze amino acids,[38] fatty acids,[39] and organic or inorganic ions.[40–45] A new contactless conductivity detector (CCD) was introduced by Zemann et al.[46]

Synthetic polyelectolytes like polyacrylic acids (PAA) or polymethacrylic acids in general do not exhibit sufficiently high absorbance to be properly detected by UV absorption at low concentration levels. Polyacrylic acids have been measured by Castignolles et al. using a diode array detector, however, these samples were prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization and exhibited a higher UV absorption due to the RAFT end group.[47] Other separations of PAA homopolymers in polymer and copolymer formulations have been presented by Cottet and coworkers.[48–50]

In this article, we demonstrate the development of a sensitive indirect UV detection method and a sensitive conductivity detection method for the determination of synthetic copolymers and blends of copolymers and homopolymers separated by CE. For these separations and detection methods an amphoteric buffer system was used.

THEORY

Indirect UV Detection (IUV)

Indirect UV detection in CE is a method based on the addition of strong UV-absorbing co-ions to the background electrolyte (BGE). These co-ions, which generate a high background absorbance, co-migrate with the nonabsorbing analyte. Because of a displacement of absorbing co-ions through the nonabsorbing analyte when passing the detector, a negative absorbance signal appears. The concentration change ($\Delta[B]$) of the co-ion because of the displacement by an analyte concentration $[A]$ can be calculated according to the Kohlrausch theory[41]:

$$\frac{\Delta[B]}{[A]} = -\frac{\mu(B)|\mu(A) + \mu(C)|}{\mu(A)|\mu(B) + \mu(C)|} \tag{1}$$

where μ describes the effective mobility of the analyte (A), the co-ion (B), and the counter ion (C). Equation (1) shows that the maximum peak intensity will be obtained by a 1 : 1 displacement. This will occur only when the analyte has the same mobility as the co-ion. Figure 1(a) shows a scheme of the IUV detection, and Figure 1(b) displays the different peak shapes in dependence on the electrophoretic mobilities of the analyte and the co-ion.

Therefore, in an indirect UV detection system, the co-ion should have the same charge and mobility as the analyte. These requirements are much easier to fulfill for small inorganic or organic ions than for polyelectrolytes, which usually exhibit a molar mass distribution. This leads to the fact that strictly speaking for evenly charged low molar mass polyelectrolytes normally only one oligomer could match the mobility of the co-ion.

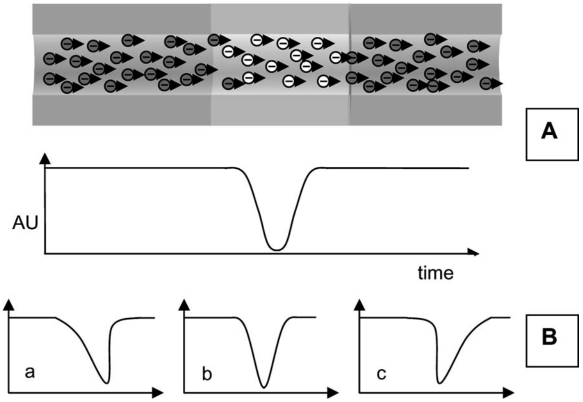

Figure 1. Scheme of the indirect UV detection (A) and peak shapes in dependence on the different mobilities (B), a: $\mu_{co-ion} > \mu_{analyte}$, b: $\mu_{co-ion} = \mu_{analyte}$, c: $\mu_{co-ion} < \mu_{analyte}$; analyte ions (white), co-ions (dark).

Contactless Conductivity Detection

The contactless conductivity detector (CCD) was introduced by Zemann and coworkers.[46,51–53] This detector is made of two electrodes that are placed cylindrically around the capillary and are connected to an AC oscillator and an amplifier. The distance between the electrodes is the detection gap. The electrodes work as capacitors and the detection gap as a resistance. When an analyte with a different conductivity from that of the BGE passes the detection gap, the change of conductivity generates a signal. The electrodes of the contactless conductivity detector are different from those in normal conductivity detection where the electrodes are in contact with the solution. The conductivity detector can be used simultaneously with a standard UV detector. Conductivity detection is based on the difference in conductance between the analyte and the BGE. Thus, a good signal/noise ratio will be obtained when there is a great difference in conductance between the analyte and the BGE. This leads to a dilemma for conductivity detection, since high separation efficiency is obtained when matching the electrophoretic mobilities for the analyte and the BGE. To overcome this dilemma BGEs based on amphoteric buffers have been used.[53,54] These buffers generate low background conductivities for a sufficient signal/noise ratio and can thus be used at considerably higher ionic strength for good separation efficiency.

EXPERIMENTAL SECTION

Chemicals and Samples

All chemicals used were of analytical grade purity. Demineralized water was obtained from a Millipore Simplicity 185 system (Millipore, Eschborn, Germany). L(+)-arginine and hexadienoic acid (sorbate) were purchased from Acros Organics (Geel, Belgium). Sodium hydroxide was purchased from Merck (Darmstadt, Germany). Poly(methacrylic acid) sodium salt (PMAA75k) ($M_w = 75\,kg/mol$) was purchased from Polymer Standards Service (Mainz, Germany). The PEG-MAA copolymers were laboratory products of BASF (Ludwigshafen, Germany). They were prepared by copolymerization of methacrylic acid (MAA) and a polyethylene oxide macromonomer (50% by weight aqueous solution of methoxy polyethylene gycol monomethacrylate with a number-average molar mass of 1000 g/mol). The macromonomer (MPEG-MM) was synthesized from polyethylene glycol monomethylether (MPEG) and MAA. The copolymerization of MAA and the macromonomer was initiated with the free-radical initiator sodium peroxodisulfate. The methacrylic acid content of the copolymers was 10% (sample 1), 20% (sample 2), or 30% by weight (sample 3). The average molar mass M_w was roughly 40 kg/mol for all copolymers. For the CE experiments the copolymer sample solutions were prepared at concentrations of 10 g/L in water. The PMAA sample solution was prepared at a concentration of 3 g/L in water.

Capillary Electrophoresis

All CE experiments were performed on a Beckmann Coulter P/ACE-MDQ instrument with diode array detection (Beckmann Coulter GmbH, Krefeld, Germany). Fused silica capillaries with an inner diameter (ID) of 50 or 75 μm and an outer diameter (OD) of 360 μm were purchased from CS-Chromatographie Service GmbH (Langerwehe, Germany). New capillaries were conditioned with 1 M NaOH for 10 min, 0.1 M NaOH for 10 min, and water for 5 min. Between the runs they were flushed with about two capillary volumes of 0.1 M NaOH and two capillary volumes of separating electrolyte. Sample introduction was performed applying pressure injections at 0.3 psi on the inlet side.

Contactless Conductivity Detector

The conductivity detection was performed with a TraceDec contactless conductivity detector (Innovative Sensor Technologies GmbH, Strasshof, Austria). The detector was adjusted at a distance of 15 cm to the capillary end and 5 cm in front of the UV detector.

RESULTS AND DISCUSSION

Indirect UV Detection

Standard electrolytes used in CE like borate, phosphate, or TRIS (trishydroxymethyl aminomethane) buffers generate high background conductivity. Therefore, they are not suitable for conductivity detection. A good alternative to these electrolytes are amphoteric buffers like arginine/sorbate (AS), histidine/sorbate (HS), or MES/arginine (MA). Mayrhofer et al. showed that the arginine/sorbate buffer worked very well for the conductivity detection of inorganic anions.[51] In a previous study, we found that the arginine/sorbate buffer works well as a background electrolyte for the separation of synthetic polyelectrolytes by CE with conductivity detection.[56] In this work we demonstrate that this AS buffer is also a suitable electrolyte for indirect UV detection of non-UV-absorbing copolymers.

The present copolymers were prepared by copolymerization of methacrylic acid (MAA) and a polyethylene oxide macromonomer. The macromonomer (MPEG-MM) was synthesized from polyethylene glycol monomethylether (MPEG) and MAA. The copolymerization of MAA and the macromonomer was initiated with the free-radical initiator sodium peroxodisulfate. The resulting copolymers are distributed in at least three parameters: (1) the total molar mass, (2) the copolymer composition, and (3) the chain length of the PEO grafts. In addition, the copolymer can be contaminated by small amounts of the homopolymers polymethacrylic acid (PMAA) and P(MPEG-MM).[55]

The resulting copolymer chemical structure is shown in Figure 2. Three copolymers with MAA contents of 10% by weight (sample 1), 20% by weight (sample 2), and 30% by weight (sample 3) were investigated.

The following separations were carried out in an uncoated fused silica capillary with 50 μm ID and a total length of 30 cm. The effective separation length for the CCD was 15 cm and for the UV detector it was 20 cm. The applied separation voltage was 10 kV. As a BGE we used a 24 mM arginine and 12 mM sorbate buffer adjusted at pH 9.

Figure 3 shows the overlay of the electropherograms for copolymers 1–3. The copolymers elute between 4 and 6 min. As can be seen, the separation of the copolymers is according to the different MAA contents and, therefore, to the different charge densities. The charge density and, hence, the electrophoretic mobility increase with increasing MAA content. In the presence of the electroosmotic flow

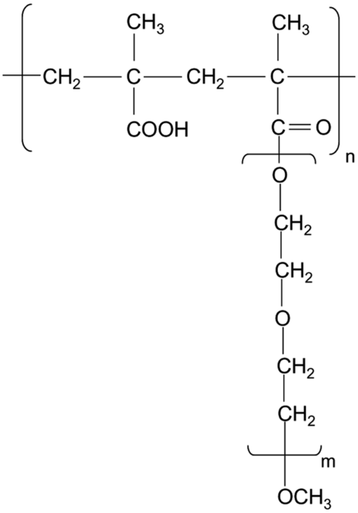

Figure 2. Chemical structure of the PEG-MAA copolymers.

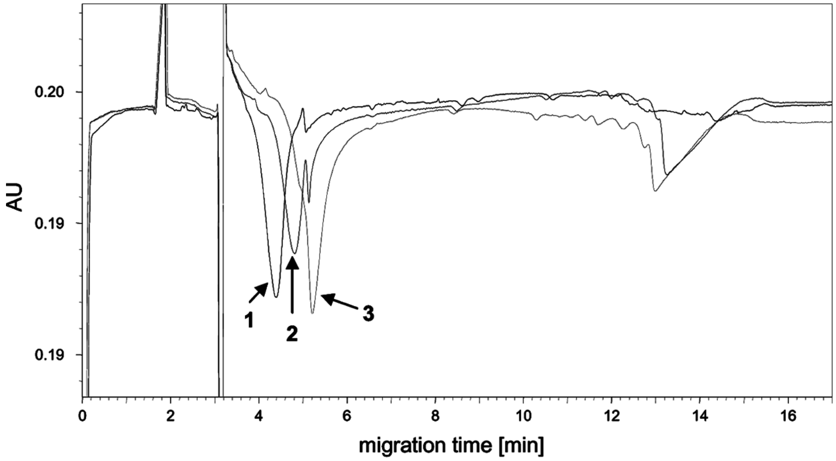

Figure 3. Electropherograms of the copolymers 1 (10% MAA), 2 (20% MAA), and 3 (30% MAA) with indirect UV detection; capillary: 50 μm ID; total length: 30 cm; uncoated fused silica; buffer: 24 mM arginine/12 mM sorbate; pH 9; voltage: 10 kV; injection: 10 s × 0.3 psi; detection: UV at 254 nm; temperature: 20°C.

(EOF), the apparent or measured mobility is the sum of the analyte mobility and the mobility of the EOF. In the present separation mode, the vectors of the mobilities are complementary. Thus, the copolymer with the lowest charge density elutes first. Another peak pattern is observed in the time range of 10 to 15 min, the main peak eluting at 13 min. The intensity of this peak series increases with increasing MAA content in the copolymer. This could be an indication that these peaks are due to MAA homopolymer fractions that are formed in addition to the copolymer. Nonreacted PEG will elute with the EOF at 3.1 min and, therefore, is difficult to detect.

Conductivity Detection

Contactless conductivity detection is another alternative detection method for non-UV-absorbing polyelectrolytes. The measured signal in conductivity detection is the difference in conductivity between the analyte and the BGE. Therefore, a buffer with low conductivity is required. Because of its low conductivity, the arginine/sorbate buffer used for the indirect UV detection is also used for conductivity detection. The following separations were carried out in an uncoated fused silica capillary with 75 μm ID and a total length of 57 cm. The effective separation length for the CCD was 42 cm and for the UV detector it was 47 cm. The applied separation voltage was 7 kV. The concentration of the AS buffer was 30 mM arginine and 15 mM sorbate. Figure 4 shows the electropherogram for copolymer 3 (30% MAA).

Figure 4 shows an electropherogram for the copolymer that is very similar to the one in Figure 3. Because of the higher buffer concentration and the larger capillary length the signals are shifted to higher migration

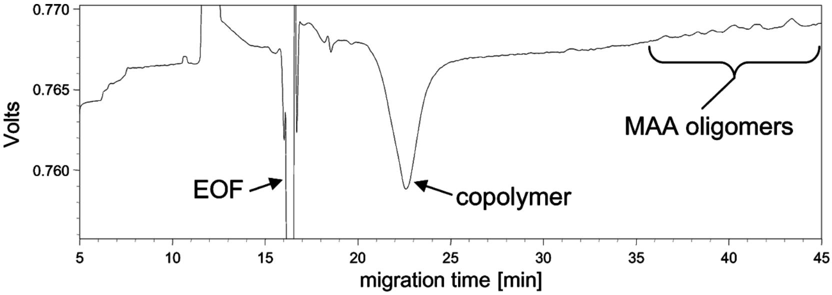

Figure 4. Electropherogram for copolymer 3 with CCD; capillary: 75 μm ID; total length: 57 cm; uncoated fused silica; buffer: 30 mM arginine/15 mM sorbate; pH 9; voltage: 7 kV; injection: 10 s × 0.3 psi; temperature: 20°C.

times. In this case, the broad intensive copolymer peak is detected at 23 min and the additional peak series from 35 to 45 min. In contrast to the IUV detection, the suspected PMAA peak series exhibits a positive detector response while the copolymer peak is negative. The change in conductivity when an analyte ion passes the detection gap is based on a displacement of BGE ions by the analyte. An equal volume of evenly charged BGE ions is displaced by the hydrodynamic volume of the copolymer. Because of the fact that the copolymer consists of 70% by weight of uncharged PEG units, the conductivity decreases when the sample passes the detector and a negative signal is obtained. The positive signals for the MAA oligomers are the result of the analyte conductivity being higher than BGE conductivity. This indicates that fully charged PMAA homopolymers generate a higher charge density per displaced volume.

To investigate the results in terms of the peak assignment and direction we analyzed blends prepared from copolymer 3 and different concentrations of a high molar mass poly(methacrylic acid) sodium salt sample (PMAA75k) with a molar mass of 75 kg/mol. The compositions of the blends are shown in Table I.

The results of these separations are shown in Figure 5.

In the electropherograms, all blend components can be identified. Copolymer 3 appears as a negative peak at a migration time of about 23 min, followed by the positive peak of PMAA75k at about 29 min. At migration times higher than 35 min, the MAA oligomers are eluted. The peak intensity of the PMAA75k increases with increasing concentration, while the intensities of the copolymer and the MAA signals remain constant. As a result of these experiments, it can be stated that evenly charged homopolymers increase the conductivity and positive signals are obtained, while mainly uncharged copolymers reduce the conductivity of the system.

Another separation of blends 1 to 4 was carried out by indirect UV detection. The experimental conditions were the same as for the CCD experiments. Figure 6 shows the results of these separations.

Table I. Composition of blends 1 to 4

Blend	Copolymer 3 concentration [g/L]	PMAA75k concentration [g/L]
1	4	—
2	4	0.75
3	4	1.5
4	4	2.25

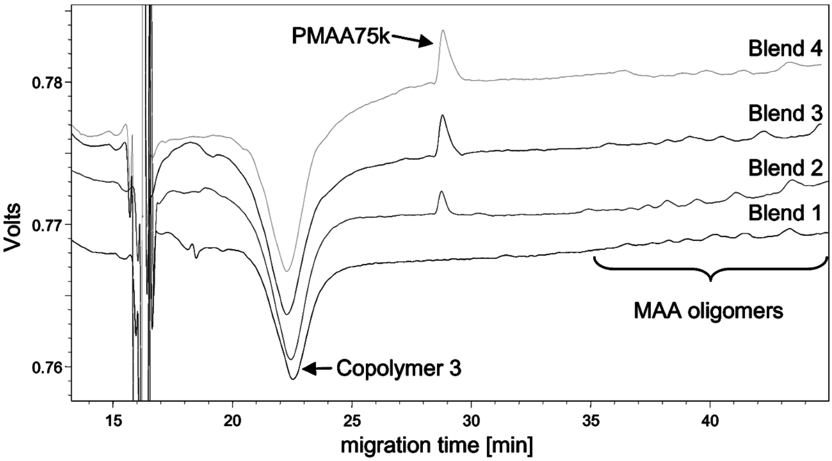

Figure 5. Electropherograms of blends 1 to 4 with conductivity detection; capillary: 75 μm ID; total length: 57 cm; uncoated fused silica; buffer: 30 mM arginine/15 mM sorbate; pH 9; voltage: 7 kV; injection: 10 s × 0.3 psi; temperature: 20°C.

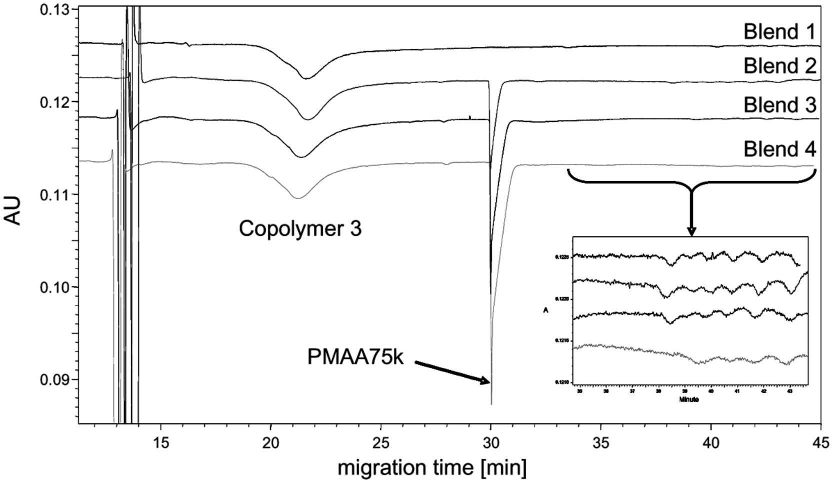

Figure 6. Electropherograms of blends 1 to 4 with indirect UV detection; capillary: 75 μm ID; total length: 57 cm; uncoated fused silica; buffer: 30 mM arginine/15 mM sorbate; pH 9; voltage: 7 kV; injection: 10 s × 0.3 psi; temperature: 20°C.

With indirect UV detection only negative signals were obtained for all analytes.

As in Figure 5, the copolymer peak appears at 23 min, the additional MAA oligomer signals are between 35 and 45 min, and the PMAA75k peak appears at 30 min. As can be seen in Figure 6, the analyte peaks are much more intensive for the IUV detection than for the CCD. This result is based on the fact that the difference in the extinction coefficient between the BGE and the analytes is larger than the difference of the conductivities measured in CCD.

CONCLUSION

Capillary electrophoresis has proven to be a feasible tool for the separation of synthetic copolymers according to their charge density. Using an amphoteric arginine/sorbate buffer and an uncoated silica capillary it was possible to develop indirect UV detection and contactless conductivity detection as alternative separation and detection methods for non-UV-absorbing analytes. With the use of such an electrolyte, high separation efficiencies and good signal/noise ratios were obtained. Although with IUV detection more intensive signals were achieved, CCD provides additional information for the identification of the analyte peaks. Because of the different peak directions, it is possible to distinguish between copolymers and homopolymers.

REFERENCES

[1] Horn, R. G. (1990). Surface forces and their action in ceramic materials. *J. Am. Ceram. Soc.* **73**, 1117–1135.

[2] Israelachvili, J. N. (1990). *Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems*. London: Academic Press.

[3] Landers, J. P. (1997). *Handbook of Capillary Electrophoresis*, 2nd ed. Boca Raton, Fla.: CRC Press.

[4] Haddad, P. R. (1997). Comparison of ion chromatography and capillary electrophoresis for the determination of inorganic ions. *J. Chromatogr. A* **770**, 281–290.

[5] Jorgensen, J. W. and K. D. Lukacs. (1981). Zone electrophoresis in open-tubular glass capillaries. *Anal. Chem.* **53**, 1298–1302.

[6] Righetti, P. G. (1996). *Capillary Electrophoresis in Analytical Biotechnology*. Boca Raton, Fla.: CRC Press.

[7] Camilleri, P., ed. (1998). *Capillary Electrophoresis: Theory and Practice*. Boca Raton, Fla.: CRC Press.

[8] Khaledi, M. G. (1998). *High Performance Capillary Electrophoresis*. New York: John Wiley.

[9] Mitchelson, K. R. and J. Cheng. (2001). *Capillary Electrophoresis of Nucleic Acids*. Totowa, N. J.: Humana Press.

[10] Grossmann, P. D. and D. S. Soane. (1991). Experimental and theoretical studies of DNA separations by capillary electrophoresis in entangled polymer solutions. *Biopolymers* **31**, 1221–1228.

[11] Bullock, J. (1993). Application of capillary electrophoresis to the analysis of polydisperse polymers. *J. Chromatogr. A* **645**, 169.

[12] Wallingford, R. A. (1996). Oligomeric separation of ionic and nonionic ethoxylated polymers by capillary gel electrophoresis. *Anal. Chem.* **68**, 2541–2548.

[13] Hoagland, D. A., D. L. Smisek, and D. Y. Chen. (1996). Gel and free solution electrophoresis of variably charged polymers. *Electrophoresis* **17**, 1151–1160.

[14] Hoagland, D. A., E. Arvanitidou, and C. Welch. (1999). Capillary electrophoresis measurements of the free solution mobility for several model polyelectrolyte systems. *Macromolecules* **32**, 6180–6190.

[15] Cottet, H., P. Gareil, O. Theodoly, and C. E. Williams. (2000). A semi empirical approach to the modeling of the electrophoretic mobility in free solution: Application to polystyrenesulfonates of various sulfonation rates. *Electrophoresis* **21**, 3529.

[16] Poli, J. B. and M. R. Schure. (1992). Separation of poly(styrene sulfonates) by capillary electrophoresis with polymeric additives. *Anal. Chem.* **64**, 896.

[17] Clos, H. N., and H. Engelhardt. (1998). Separations of anionic and cationic synthetic polyelectrolytes by capillary gel electrophoresis. *J. Chromatogr. A* **802**, 149–157.

[18] Minárik, M., B. Gǎs, and E. Kenndler. (1997). Size-based separation of polyelectrolytes by capillary zone electrophoresis: Migration regimes and selectivity of poly(styrenesulphonates) in solutions of derivatized cellulose. *Electrophoresis* **18**, 98–103.

[19] Cottet, H. and P. Gareil. (1997). Electrophoretic behaviour of fully sulfonated polystyrenes in capillaries filled with entangled polymer solutions. *J. Chromatogr. A* **772**, 369.

[20] Cottet, H., P. Gareil, and J.-L. Viovy. (1998). The effect of blob size and network dynamics on the size-based separation of polystyrenesulfonates by capillary electrophoresis in the presence of entangled polymer solutions. *Electrophoresis* **19**, 2151.

[21] Cottet, H. and P. Gareil. (2002). Size-based separation of synthetic polyelectrolytes in entangled polymer solution capillary electrophoresis: The effect of binary mixtures of separating polymers differing in molecular mass. *Electrophoresis* **23**, 2788.

[22] Kok, W. T., R. Stol, and R. Tijssen. (2000). Electrokinetic separations for synthetic polymers. *Anal. Chem.* **72**, 468A.

[23] Engelhardt, H. and O. Grosche. (2000). Capillary electrophoresis in polymer analysis. *Adv. Polym. Sci.* **150**, 189–217.

[24] Engelhardt, H. and M. Martin. (2004). Characterization of synthetic polyelectrolytes by capillary electrophoretic methods. *Adv. Polym. Sci.* **165**, 211–247.

[25] Oudhoff, K. A., F. A. van Damme, E. P. C. Mes, P. J. Schoenmakers, and W. T. Kok. (2004). Characterization of gycerin-based polyols by capillary electrophoresis. *J. Chromatogr. A* **1046**, 263–269.

[26] Cottet, H. and P. Gareil. (2000). From small charged molecules to oligomers: A semi empirical approach to the modeling of actual mobility in free solution. *Electrophoresis* **21**, 1493.

[27] Braud, C., R. Devarieux, A. Atlan, C. Ducos, and M. Vert. (1998). Capillary zone electrophoresis in normal or reversed polarity separation modes for the analysis of hydroxy acid oligomers in neutral phosphate buffer. *J. Chromatogr. A* **706**, 73–82.

[28] Cottet, H. and P. Gareil. (2001). Capillary electrophoresis of associative diblock copolymers. *J. Chromatogr. A* **939**, 109.

[29] Grosche, O., J. Bohrisch, U. Wendler, W. Jaeger, and H. Engelhardt. (2000). Characterization of synthetic polyelectrolytes by capillary electrophoresis. *J. Chromatogr. A* **894**, 105–116.

[30] Collet, J., C. Tribet, and P. Gareil. (1996). Use of neutral surfactants for the capillary electrophoresis separation of hydrophobically modified poly(acrylic acids). *Electrophoresis* **17**, 1202.

[31] Cottet, H., C. Simo, W. Vayaboury, and A. Cifuentes. (2005). Non-aqueous and aqueous capillary electrophoresis of synthetic polymers. *J. Chromatogr. A* **1068**, 59–73.

[32] Cottet, H. and P. Gareil. (2008). Separation of synthetic (co)polymers by capillary electrophoresis techniques. In *Capillary Electrophoresis: Methods and Protocols*, ed. P. Schmitt-Kopplin. Totowa, N.J.: Humana Press.

[33] Hjertén, S., K. Elenbring, F. Kilár, J.-L. Liao, A. J. C. Chen, C. J. Siebert, and M.-D. Zhu. (1987). Carrier-free zone electrophoresis, displacement electrophoresis and isoelectric focusing in a high-performance electrophoresis apparatus. *J. Chromatogr.* **403**, 47–61.

[34] Röder, A. and K. Bächmann. (1995). Simultaneous determination of organic and inorganic anions in the sub-μmol/l range in rain water by capillary zone electrophoresis. *J. Chromatogr. A* **689**, 305–311.

[35] Wu, C. H., Y. S. Lo, Y. H. Lee, and T. I. Lin. (1995). Capillary electrophoretic determination of organic acids with indirect detection. *J. Chromatogr. A* **716**, 291–301.

[36] Lu, B. and D. Westerlund. (1996). Indirect UV detection of carbohydrates in capillary zone electrophoresis by using tryptophan as a marker. *Electrophoresis* **17**, 325–332.

[37] Stefani, M., C. Negrell, C. Braud, and M. Vert. (1999). Capillary zone electrophoretic analysis of positively charged poly(ethylene oxide) macromolecules using non-covalent polycation-coated fused-silica capillary and indirect UV detection. *J. Chromatogr. A* **864**, 335–344.

[38] Olefirowicz, T. M. and A. G. Ewing. (1990). Capillary electrophoresis with indirect amperometric detection. *J. Chromatogr.* **499**, 713–719.

[39] Erim, F. B., X. Xu, and J. C. Kraak. (1995). Application of micellar electrokinetic chromatography and indirect UV detection for the analysis of fatty acids. *J. Chromatogr. A* **694**, 471–479.

[40] Foret, F., S. Fanali, L. Ossicini, and P. Bocek. (1989). Indirect photometric detection in capillary zone electrophoresis. *J. Chromatogr.* **470**, 299.

[41] Nielen, M. W. F. (1991). Quantitative aspects of indirect UV detection in capillary zone electrophoresis. *J. Chromatogr.* **588**, 321–326.

[42] Weiss, C. S., J. S. Hazlett, M. H. Datta, and M. H. Danzer. (1992). Determination of quaternary ammonium compounds by capillary electrophoresis using direct and indirect UV detection. *J. Chromatogr.* **608**, 325–332.

[43] Barger, W. R., R. L. Mowery, and J. R. Wyatt. (1994). Separation and indirect detection by capillary zone electrophoresis of ppb (w/w) levels of aluminum ions in solutions of multiple cations. *J. Chromatogr. A* **680**, 659–665.

[44] Rhemrev-Boom, M. M. (1994). Determination of anions with capillary electrophoresis and indirect ultraviolet detection. *J. Chromatogr. A* **680**, 675–684.

[45] Li, Q. and E. S. Yeung. (1994). *J. Cap. Electrophor.* **1**, 55.

[46] Zemann, A. J., E. Schnell, D. Volgger, and G. K. Bonn. (1998). Contactless conductivity detection for capillary electrophoresis. *Anal. Chem.* **70**, 563–567.

[47] Castignolles, P., M. Gaborieau, E. Hilder, E. Sprong, J. C. Ferguson, and R. G. Gilbert. (2006). High-resolution separation of oligo(acrylic acid) by capillary zone electrophoresis. *Macromol. Rapid Commun.* **27**, 42–46.

[48] Jacquin, M., P. Muller, R. Talingting-Pabalan, H. Cottet, J. F. Berret, T. Futterer, and O. Théodoly. (2007). Chemical analysis and aqueous solution properties of charged amphiphilic block copolymers PBA-*b*-PAA synthesized by MADIX. *J. Colloid Interface Sci.* **316**, 897–911.

[49] Jacquin, M., P. Muller, G. Lizaraga, C. Bauer, H. Cottet, and O. Théodoly. (2007). Characterization of amphiphilic diblock copolymers synthesized by MADIX polymerization process. *Macromolecules* **40**, 2672–2682.

[50] Morel, A., H. Cottet, M. In, S. Deroo, and M. Destarac. (2005). Electrophoretic behavior of amphiphilic diblock copolymer micelles. *Macromolecules* **38**, 6620–6628.

[51] Mayrhofer, K., A. J. Zemann, E. Schnell, and G. K. Bonn. (1999). Capillary electrophoresis and contactless conductivity detection of ions in narrow inner diameter capillaries. *Anal. Chem.* **71**, 3828–3833.

[52] Hilder, E. F., A. J. Zemann, M. Macka, and P. R. Haddad. (2001). Anion-exchange capillary electrochromatography with indirect UV and direct contactless conductivity detection. *Electrophoresis* **22**, 1273–1281.

[53] Zemann, A. J. (2003). Capacitively coupled contactless conductivity detection in capillary electrophoresis. *Electrophoresis* **24**, 2125–2137.

[54] Guijt, R. M., C. J. Evenhuis, M. Macka, and P. R. Haddad. (2004). Conductivity detection for conventional and miniaturised capillary electrophoresis systems. *Electrophoresis* **25**, 4032–4057.

[55] Adler, M., F. Rittig, S. Becker, and H. Pasch. (2005). Multidimensional chromatographic and hyphenated techniques for hydrophilic copolymers. 1. Analysis of comb-like copolymers of ethylene oxide and methacrylic acid.*Macromol. Chem. Phys.* **206**, 2269.

[56] Spriestersbach, K.-H., F. Rittig, and H. Pasch. (2008). Separation of non UV-absorbing synthetic polyelectrolytes by capillary electrophoresis with contactless conductivity detection. *Electrophoresis* **29**, 4407–4411.