Poly(tetrafluoroethylene) separation capillaries for capillary electrophoresis
Properties and applications

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Abstract

Poly(tetrafluoroethylene) (PTFE) is a material widely known for its inertness and excellent electrical properties. It is also transparent in the UV region and has a reasonable thermal conductivity. These properties make PTFE a suitable material for the separation capillary in capillary electrophoresis. Differences in the chemistry of the capillary wall compared to fused silica (FS) can make PTFE an interesting alternative to FS for some special applications. In this work, properties of a commercial PTFE capillary of approx. 100 μm i.d. were investigated, including the dependence of electroosmotic flow (EOF) on pH for unmodified and dynamically modified PTFE, optical properties, and practical aspects of use. The main problems encountered for the particular PTFE capillary used in this study were that it was mechanically too soft for routine usage and the crystallinity of the PTFE caused light scattering, leading to high background absorbance values in the low UV region. The profile of the EOF versus pH for bare PTFE surprisingly showed significantly negative EOF values at pH <4.2, with an EOF of $-30 \times 10^{-9}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$ being observed at pH 2.5. This is likely to be caused by either impurities or additives of basic character in the PTFE, so that after their protonation at acidic pH they establish a positive charge on the capillary wall and create a negative EOF. A stable cationic semi-permanent coating of poly(diallyldimethylammonium chloride) (PDDAC) could be established on the PTFE capillary and led to very similar magnitudes of EOF to those observed with FS. A hexadecanesulfonate coating produced a cathodic EOF of extremely high magnitude ranging between $+90$ and $+110 \times 10^{-9}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$, which are values high enough to allow counter-EOF separation of high mobility inorganic anions. In addition, pH-independent micellar electrokinetic capillary chromatography (MEKC) separations could be easily realised due to hydrophobic adsorption of sodium dodecylsulfate (used to form the micelles) on the wall of the PTFE capillary. The use of polymers that would be mechanically more robust and optically transparent in the low-UV region should make such CE capillaries an interesting alternative to fused silica.
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1. Introduction

The separation capillary in capillary electrophoresis (CE) plays a crucial role in the separation as it is inside this capillary where analytes separate under the imposed separation voltage [1]. The capillary should satisfy a number of criteria. It should have suitable mechanical properties, be an excellent electrical insulator, be able to withstand high electrical field strengths, and should possess a high thermal conductivity to allow effective heat dissipation. The capillary should also be transparent over the entire UV-Vis spectral range, and it should be optically clear to prevent light scattering leading to large values of background absorbance. Finally, the capillary should have well-defined surface characteristics giving reproducible electroosmotic flow (EOF), and the surface chemistry should be well-understood so that EOF can be varied in a controllable manner.

The advent of the fused silica (FS) capillary in the late 1970s [2] not only revolutionised gas chromatography in

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its capillary format [3], but it also enabled the development of capillary liquid chromatography, capillary electrophoresis and capillary electrochromatography. The technology for making fused silica capillaries has been perfected over the years [4]. From the early stages of CE, polyimide-coated fused silica capillaries have dominated because of their ready availability and excellent properties. Not surprisingly an overwhelming percentage of CE separations (close to 100%) is realised using fused silica capillaries. Probably the only significant practical disadvantage in its general use in CE with optical detection is the need to remove some of the polyimide coating to make a detection window, with the associated problem that this section of the capillary becomes very fragile. Although this problem can be addressed to some degree by applying UV-transparent protective coating, the fragility of the capillary persists. Chemically, FS has the advantage of a material that has been in use over decades and consequently its surface chemistry has been well researched. In CE, FS capillaries are mostly used in the bare, unmodified condition, although FS modified with a neutral hydrophilic coating is often a requirement for separations of biopolymers and especially of proteins [5]. The unmodified FS surface can also be undesirable when the ion-exchange properties of silica [6] can cause adsorption of ligands in the presence of metal ions in the electrolyte [7,8] or of metal ions themselves [9,10].

Although polymer materials have captured a significant percentage of the CE-on-a-chip microfluidic devices [11,12], somewhat surprisingly the use of polymeric separation capillaries in CE has remained limited to a dozen or so reports over the last 20 years. Poly(tetrafluoroethylene) (PTFE) has been the polymer used most frequently [13–22] and it seems that its use as large diameter capillaries (~200 μm) in the early papers may have originated from the previous use of about 200 μm i.d. PTFE capillaries in capillary isotachophoresis (cITP) [23]. Some other polymers have also been investigated. Polypropylene (PP) capillaries with a variety of hydrophilic surface modifications or poly(methyl methacrylate) (PMMA) have been utilised by Lee and co-workers, mainly for separations of proteins [24–28]. Ethylene vinyl acetate copolymer was used for the separation of porphyrins with photometric detection [29]. Schneider and Engelhardt used polyether ether ketone (PEEK) and PMMA capillaries with an inserted quartz detection window for photometric detection, or with on-capillary fluorimetric detection [30].

Polymer capillaries can potentially have some advantages over FS, such as lower cost and a different surface chemistry. Theoretically, neutral polymers (including PTFE) should possess no charged groups, although in reality they are known to contain some surface carboxylic groups formed by oxidation, especially under the influence of UV light and/or ozone [31]. Several polymers, such as PTFE, are transparent at short-wavelength-UV, even though impurities and crystallinity may cause scattering of UV light [32]. It should be also noted that the unusually low refractive index

of PTFE makes it a unique material for construction of totally reflecting photometric detection cells, or liquid core waveguides [18,33]. Polymer capillaries are typically also very good electrical insulators and are inert and thermally stable [34]. It should be mentioned that PTFE tubing and capillaries have been used extensively for a range of analytical instruments, so a large variety of these materials having a broad range of inner and outer diameters is generally available, although capillaries of diameters similar to those of FS capillaries used in CE have somewhat broadly specified diameters and are clearly not made for this purpose.

In this study the applicability of a commercially available PTFE capillary of approx. 100 μm i.d. as a CE capillary is evaluated. Mechanical and physical properties and aspects of practical use are evaluated, and EOF is studied for a number of capillary wall chemistries including unmodified and modified PTFE.

2. Experimental

2.1. Instrumentation

Two different instrumental CE configurations were used: (i) A Waters Capillary Ion Analyser fitted with Millenium data processing software (Milford, MA, USA) was used with capillaries of 0.600 m total length and length to detector 0.520 m. Injections were performed hydrostatically at a height of 100 mm used with various injection times. (ii) An Agilent Technologies [3D]CE (Waldbron, Germany) was used with capillaries of 0.485 m total length and length to detector 0.400 m, or 0.400 m total length and length to detector 0.320 m (see figure captions). Injections were performed hydrodynamically at a pressure of 20 mbar used with 2 s injection time unless specified otherwise. Spectra of PTFE and FS capillaries were both measured relative to air as a reference.

2.2. Chemicals and materials

All chemicals used were of Analytical Reagent grade. Water was treated with a Millipore (Bedford, MA, USA) Milli-Q water purification system.

The fused silica capillaries were purchased from Polymicro (Phoenix, AZ, USA). The PTFE capillary was purchased from Cole-Parmer (Vernon Hills, IL, USA, No. 06417-72).

2.3. Procedures

2.3.1. CE measurements

All solutions and electrolytes were degassed using vacuum sonication and filtered through a 0.45 μm syringe filter (Activon Thornleigh, Australia) before use.

Absorbance values in Table 1 were measured for PTFE compared to FS, with both capillaries being filled with water. Stray light values were measured using a Na_2CrO_4 solution

Table 1
Optical properties of PTFE compared to FS

Property	FS		PTFE	
	254 nm	654 nm	254 nm	654 nm
Absorbance (AU)	– (Reference)	– (Reference)	1.1	0.01
Stray light	1.6%	1.8%	15%	1.0%
Baseline noise (mAU)	0.06	0.04	0.13	0.04

Conditions: instrument, Waters capillary ion analyser, using a standard mercury lamp at 254 nm, or a red lead as light source as detailed in [22], for other conditions see Section 2.

at 254 nm and a methylene blue solution at 654 nm according to published procedures [39]. Baseline noise was measured with capillaries filled with a 10 mM phosphate buffer pH 7.0 and +30 kV separation voltage.

3. Results and discussion

3.1. Mechanical properties and practical aspects of usage

PTFE tubing in general, and especially those of small dimensions, are mechanically quite soft, do not hold their shape well, and are prone to coiling. These properties caused some problems depending on the instrumental configuration used. Generally, installation of the capillary in the CE instrument needed to be performed with great care to avoid mechanical damage to the capillary. With the Agilent CE a pair of fine long tweezers was required to guide the ends of the capillary into the conical holes leading to the tubular electrodes. Great care was also necessary when inserting the capillary installation into the optical detector, particularly with the Waters CE where only a minimal pressure could be used to push the capillary into the self-aligning V-groove in the optical detector unit. Experience gained with handling the PTFE capillary in these two CE instruments clearly indicated that a mechanically rigid polymer with mechanical properties more similar to those of FS capillaries is required for practical and convenient use.

3.2. Heat dissipation and measurement of effective capillary diameter

A plot of separation current versus applied voltage is generally used to determine the maximum applicable separation voltage (and corresponding current) by identifying the point where poor heat dissipation causes the plot to deviate substantially from linearity [35]. From a practical point of view, occurrence of current instability above a certain voltage or current values usually indicates significant overheating of the capillary. Detection noise as a function of the separation voltage can also be plotted to determine the separation voltage limit [36]. Fig. 1 shows plots of the separation current versus applied voltage for the PTFE capillary and also

for a 100 μm i.d. FS capillary. Additionally, derived plots of current/voltage versus applied voltage were plotted (hollow points in Fig. 1).

Two observations can be made from Fig. 1. First, the effective capillary diameter (averaged across the capillary length) for the PTFE capillary can be calculated by comparing the current/voltage values extrapolated to zero voltage, based on the known i.d. of the FS capillary ($100 \pm 1 \mu m$). The i.d. value for the PTFE capillary resulting from Fig. 1 is 137 μm. For a previously uncharacterised capillary, this is a valuable result as the capillary does not have any i.d. tolerances guaranteed by the manufacturer and measurement by optical microscopy on a cross-section might be grossly imprecise [24]. We found this method to be a simple, reliable and convenient alternative to the method of weighing capillaries filled with water [24]. Second, it is obvious that the heat dissipation for PTFE is somewhat poorer than for FS. This is to be expected, as the thermal conductivity coefficient for FS at 25 °C is 1.3 W m^{-1} K^{-1} compared to 0.26 W m^{-1} K^{-1} for PTFE [37,38]. However most importantly, the PTFE capillary did not show any serious problems related to bubble formation or electrolyte boiling, and could be used at separation currents well over 100 μA (see Fig. 1).
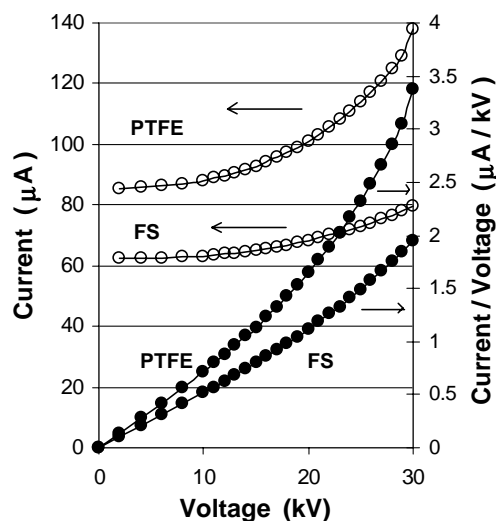

Fig. 1. Comparison of heat dissipation between FS and PTFE capillaries. Conditions: Agilent CE; electrolyte, 10 mM sodium phosphate, pH 7.0; FS capillary inner diameter, 100 μm. For other conditions see Section 2.
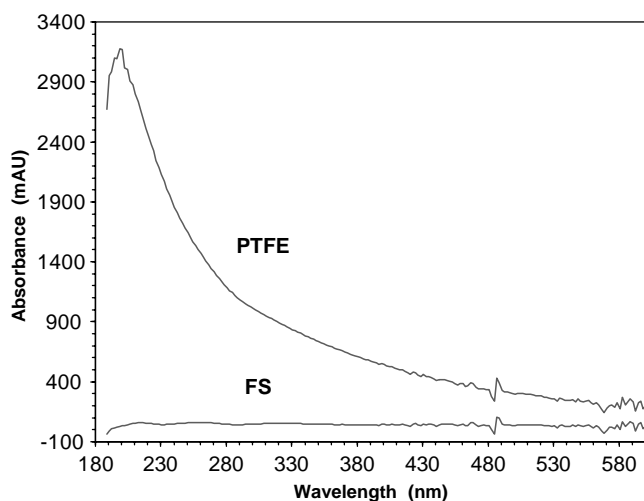
Fig. 2. Absorbance spectra of PTFE and fused silica capillaries measured using an Agilent CE fitted with a diode-array detector. Conditions: FS capillary, i.d. 100 μm, both FS and PTFE capillaries filled with water.

3.3. Optical properties

It is important to realise that the absorbance values measured in the absorption spectrum of any material will be the sum of the value of 'true' absorbance caused by absorption of light by molecules of the compound according to its electronic spectrum, and by the value of 'pseudo-absorbance' caused by light scattering. The pseudo-absorbance contribution is often significant with polymers that show crystallinity and appear opaque. The light scattering contribution increases with decreasing wavelength and is the cause of the apparent absorptivity of crystalline polymers increasing into the low-UV region [32].

This behaviour can be observed in the absorbance spectrum of the PTFE capillary measured in the diode-array spectrophotometer of the Agilent CE (Fig. 2). This is in accordance with other independent experiments conducted in the Waters Capillary Ion Analyser CE, where background absorbance, the percentage of stray light, and baseline noise under typical CE operational conditions were measured, with these results being presented in Table 1. In particular, for the PTFE capillary a background absorbance of 1.1 was measured at 254 nm (compared to FS, both capillaries filled with water), while a relatively very small absorbance (approx. 0.01) was measured for a detection wavelength of 654 nm. The assertion that the high background absorbance for PTFE at 254 nm was largely a pseudo-absorbance resulting from light scattering was supported by another series of experiments where stray light values were measured according to a procedure described earlier [39]. These experiments showed that the considerably higher amount of scattered light for PTFE at 254 nm correlated with its high background absorbance (see Table 1). As expected, the baseline noise also correlated with the levels of background absorbance.

From these observations it was evident that the crystallinity of PTFE posed a problem for detection in the
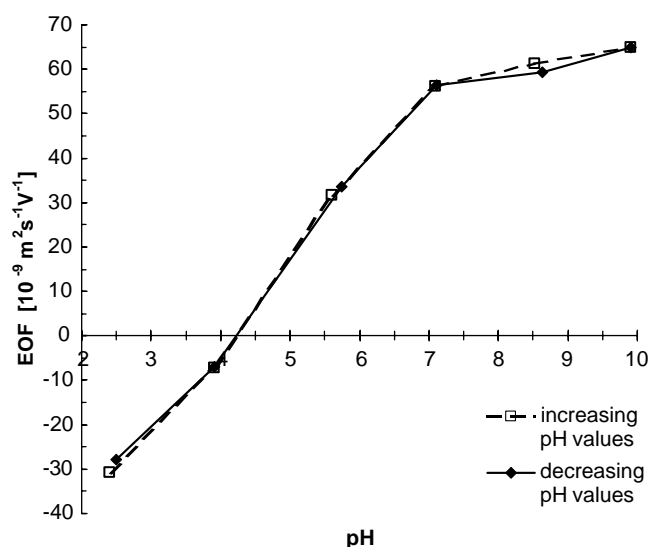

Fig. 3. Plot of EOF vs. pH for an unmodified PTFE capillary. Conditions: Agilent CE; capillary, PTFE (0.400 m × 0.320 m); electrolyte, 5 mM sodium phosphate; detection, 254 nm; EOF marker, acetone (0.1% in background electrolyte).

low-UV spectral region. For this reason, amorphous polymers (with a low degree of crystallinity), such as some of the new generation fluoropolymers [40], should be used to produce a CE capillary which is transparent in the low-UV region.

3.4. EOF characteristics of unmodified and modified PTFE and their potential as separation capillaries in CE

3.4.1. Unmodified PTFE

The profile of EOF versus pH for a PTFE capillary is shown in Fig. 3. Surprisingly, PTFE exhibited a pH dependence which was somewhat similar to that of FS, although PTFE theoretically possesses no ionisable groups. The significant cathodic EOF at pH >4.5 could be explained by the presence of surface carboxylate groups formed by oxidation under the influence of UV light and/or ozone [31]. The significant anodic (reversed) EOF at pH <4.0, reaching approx. -30×10^{-9} m^2 s^{-1} V^{-1} at pH 2.5, was even more surprising. The presence of basic compounds as impurities or additives in the PTFE which would acquire positive charge at pH <4 is a possible explanation.

The main differences in the surface chemistry of PTFE compared to FS are the hydrophobicity of PTFE [41,42] and the absence of the silanol groups densely covering the surface of FS [6]. Previously [22], thorium, uranium and lanthanum complexes with the metallochromic ligand arsenazo III were separated in a PTFE capillary which had been dynamically coated with Carbowax 20 M to suppress hydrophobic interactions, with detection being performed using a light-emitting diode at 654 nm. An improved peak shape for Th^{IV} compared to FS was observed, indicating that with PTFE, the interactions of the complex with the
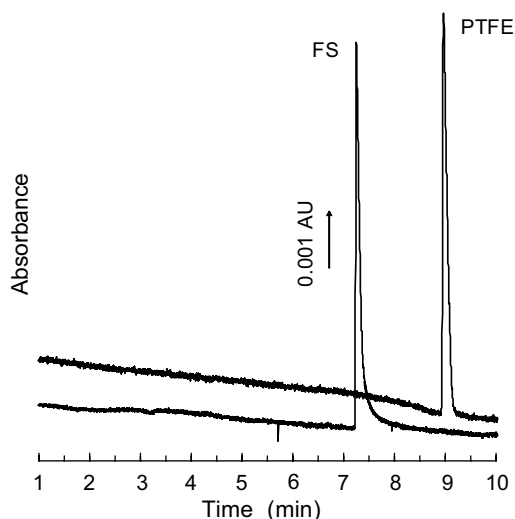
Fig. 4. Separation of Fe(III) in an acidic electrolyte in FS and PTFE capillaries. Conditions: Waters CE; capillary, (0.600 m × 0.520 m), 100 μm i.d.; electrolyte, 10 mM $HClO_4^-$ 5 mM NaOH, pH 2.4; voltage, +15 kV; detection, 254 nm; injection, 5 s hydrostatic at 100 mm; analyte concentration: 1.0 mM.

Fig. 5. Separation of anions in a PTFE capillary with reversed EOF using a sem-permanent coating of PDDAC. Conditions: Agilent CE; capillary, (0.485 m × 0.400 m), 137 μm i.d.; electrolyte, 2.5 mM CrO_4/Tris, pH 8.5; voltage, −25 kV; detection, 380 nm; injection, 5 s at 20 mbar; analyte: 0.05 mM. Capillary conditioning: before run, flushing with 1% PDDAC for 2 min, waiting for 5 min and flushing with electrolyte for 2 min. Peak identification: 1, Cl^-; 2, SO_4^{2-}; 3, NO_3^-; 4, ClO_3^-; 5, PO_4^{3-}; 6, CO_3^{2-}; 7, C_2–C_8 sulfonates.

capillary wall had been reduced. It is well known that the silanol groups of FS can cause undesirable adsorptions of metal ions onto the capillary wall [6–10], and therefore the absence of silanols in PTFE could be utilised for separations of metal cations of higher valent metals which are prone to hydrolysis and subsequent adsorption onto the silanol groups. Thornton and Fritz presented several interesting separations of metal cations including Cr^{3+}, Cu^{2+}, Fe^{3+}, UO_2^{2+}, VO^{2+}, and VO_2^+ in non-complexing acidic electrolytes based on HCl or $HClO_4$ at pH 2.3, using direct detection at 185 nm [43]. Some of the peaks obtained exhibited a degree of tailing that could be attributed to solute-wall interactions. The separation of Fe^{3+} in a $HClO_4$ electrolyte at pH 2.4 was performed on both FS and PTFE capillaries and Fig. 4 shows clearly that peak tailing was considerably reduced in the PTFE capillary. This demonstrated that PTFE capillaries have potential for separation of metal cations of higher valent metals in non-complexing electrolytes. Other polymer materials could offer similar advantages.

3.4.2. PTFE modified for anodic (reversed) EOF

Surface modifications of any capillary material are very important for the purpose of manipulation of the EOF, which is a common necessity in CE. For FS capillaries, reversal of the EOF can be achieved by the addition to the electrolyte of long chain alkyltrimethylammonium salts, such as tetradecyltrimethylammonium, to provide dynamic modification of the capillary wall [44]. Since PTFE is very hydrophobic, one would expect this approach to yield a stable layer of adsorbed alkyltrimethylammonium ions. When tetradecyltrimethylammonium ions were added to the electrolyte used with the PTFE capillary, an anodic (reversed) EOF similar to that achieved in FS under same conditions
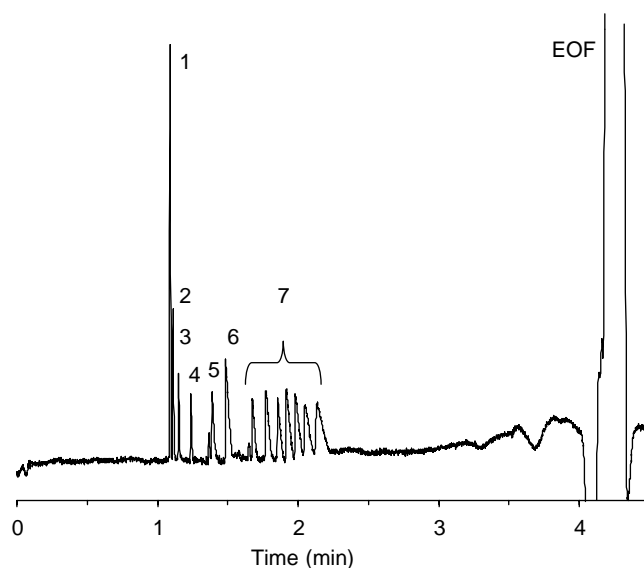
was observed initially. However, somewhat surprisingly, this coating proved to be unstable, and the reversed EOF values then gradually diminished before reverting back to cathodic EOF.

EOF reversal can also be accomplished by establishing a semi-permanent coating of a cationic polymer, such as poly(diallyldimethylammonium chloride) (PDDAC) [45,46], without the need for the additive to be maintained in the electrolyte. This approach was found to be suitable for EOF reversal in PTFE capillaries, with a stable anodic (reversed) EOF of approx. -30×10^{-9} m^2 s^{-1} V^{-1} being observed. This semi-permanent modification approach was used for the PTFE capillary, which was then applied to the separation of a range of anions using indirect photometric detection at 380 nm with a buffered chromate electrolyte [47] (Fig. 5). Symmetrical peaks and satisfactory overall separation performance (155 000 theoretical plates for chloride) of the PTFE capillary resulted for most of the analytes tested. Some electromigrational dispersion was observed for the peaks of the alkanesulfonic acids. This resulted from the relatively large amount of sample introduced into the PTFE capillary due to its large diameter (137 μm).

3.4.3. PTFE modified for pH independent cathodic EOF

Creation of a pH-independent cathodic EOF can be of advantage for the development of counter-EOF methods across a wide range of pH. This is especially true of acidic electrolytes, where the EOF would normally be very small. Dynamic modification of a PTFE capillary with
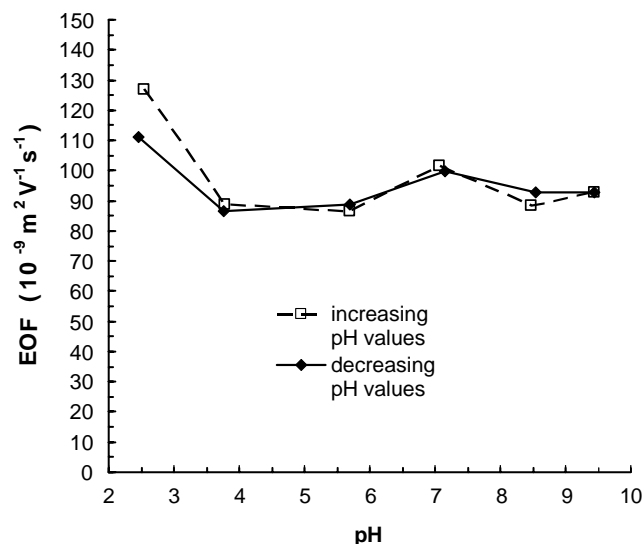
Fig. 6. Plot of EOF vs. pH for a PTFE capillary dynamically coated with hexadecane sulfonate (HdS). Electrolyte, 0.1 mM HdSNa in 5 mM phosphate–methanol (99:1, v/v); other conditions as in Fig. 3.

hexadecanesulfonate was found to create a high magnitude cathodic EOF with values in the range (90–110) $\times$ $10^{-9}\,m^2\,s^{-1}\,V^{-1}$, as illustrated in Fig. 6. Such high EOF values, which to our knowledge have not been reported previously, should not only enable relatively fast separations of anions in the counter-EOF mode, but should also make this approach applicable for the separation of highly mobile inorganic anions. The separation of a range of anions including NO_3^-, SO_4^{2-}, and Cl^- could be achieved in this way, but conventional indirect photometric detection could not be used because the addition of the anionic indirect absorption probe into the electrolyte severely diminished the magnitude of the EOF. Detection could be achieved using a cationic indirect absorption probe (4-aminopyridine) which produced so-called Kohlrausch peaks for the analyte anions. However, detection sensitivity with this approach was poor. A different detection method, such as contactless conductivity detection [48,49], might be more suitable for this application.

3.4.4. PTFE modified for pH-independent MEKC

In micellar electrokinetic chromatography (MEKC), unmodified FS capillaries are usually used, resulting in the EOF being strongly dependent on the electrolyte pH [50–52]. To provide pH-independent EOF, cationic polymer-coated capillaries have been used in MEKC with sodium dodecylsulfate (SDS) [53–56]. Adsorption of the anionic SDS onto the positively charged capillary wall by electrostatic interaction resulted in a stable layer that produced the pH-independent EOF [56].

A similar effect can be expected for a very hydrophobic capillary such as PTFE. Indeed, using electrolytes of 5 mM phosphate with 35 mM SDS and 5% *n*-butanol at pH values 3–9, a relatively pH-independent cathodic EOF was obtained, varying only between approx. 35×10^{-9} and

$+50 \times 10^{-9}\,m^2\,s^{-1}\,V^{-1}$ at pH 3 and 9, respectively. This permitted MEKC separations to be performed over the pH range of 3–9. The high background absorbance of the PTFE in the UV region necessitated the use of a 100 μm i.d. piece of FS capillary attached to the PTFE capillary just before the point of detection in the Agilent optical interface. However, the coupling of the two capillaries resulted in a poor separation efficiency (possibly due to the differences in EOF in the PTFE and the FS capillary), which again illustrated the need for an amorphous UV-transparent polymer.

4. Conclusions

PTFE has significant potential as a capillary material for CE and provides a useful alternative to the well established fused silica capillaries. For the particular PTFE capillary examined in this study, the following general conclusions could be made. First, PTFE is mechanically too soft for routine use and a much harder polymer should be sought. However, heat dissipation through the capillary did not represent a problem. Second, the opacity of the PTFE created difficulties for detection in low-UV range and therefore an amorphous UV-transparent polymer should be used. Third, the unmodified PTFE capillary showed a surprisingly significant anodic EOF at pH <4, and reversed EOF could be produced using a stable cationic semi-permanent coating of PDDAC, leading to an EOF of very similar magnitude to that obtained using a FS capillary coated in the same manner. An extremely high magnitude of cathodic EOF with values in the range between $+90$ and $+110 \times 10^{-9}\,m^2\,s^{-1}\,V^{-1}$ could be achieved by coating PTFE with hexadecanesulfonate and this was found suitable for counter-EOF separation of highly mobile inorganic anions. Finally, pH-independent MEKC separations could be performed due to the hydrophobic adsorption of SDS onto PTFE.

It can be expected that a mechanically harder and UV-transparent amorphous polymer would have significant potential as a material for CE capillaries.

References

[1] S.F.Y. Li, Capillary electrophoresis: principles, practice, and applications, Journal of Chromatography Library, vol. 52, Elsevier, Amsterdam, 1992, p. 155.
[2] R.D. Dandenau, E.H. Zerenner, J. High Resolut. Chromatogr. 1 (1979) 351.
[3] R.D. Dandenau, E.H. Zerenner, LC GC 8 (1990) 908.
[4] S. Griffin, LC GC Eur. 16 (2003) 276.

[5] A.M. Douherty, N. Cooke, P. Shieh, in: J.P. Landers (Ed.), Handbook of Capillary Electrophoresis, second ed., CRC Press, Boca Raton, FL, 1997, p. 675.

[6] R.K. Iler, The Chemistry of Silica, Wiley, New York, 1979, p. 303.

[7] B. Gassner, W. Friedel, E. Kenndler, J. Chromatogr. A 680 (1994) 25.

[8] M. Macka, P.R. Haddad, W. Buchberger, J. Chromatogr. A 706 (1995) 493.

[9] K. Salomon, D.S. Burgi, J.C. Helmer, J. Chromatogr. 559 (1991) 69.

[10] J.E. Dickens, J. Gorse, J.A. Everhart, M. Ryan, J. Chromatogr. B 657 (1994) 401.

[11] A.J. de Mello, Lab on a Chip 2 (2002) 31N.

[12] H. Becker, L.E. Locascio, Talanta 56 (2002) 267.

[13] F.E.P. Mikkers, F.M. Everaerts, Th.P.E.M. Verheggen, J. Chromatogr. 169 (1979) 11.

[14] K.D. Lukacz, J.W. Jorgenson, J. High Resolut. Chromatogr. Chromatogr. Commun. 8 (1985) 407.

[15] A. Zhu, Y. Chen, J. Chromatogr. 470 (1989) 251.

[16] T.P.E.M. Verheggen, A.C. Schoots, F.M. Everaerts, J. Chromatogr. 503 (1990) 245.

[17] A.C. Schoots, T.P.E.M. Verheggen, P.M.J.M. De Vries, Clin. Chem. 36 (1990) 435.

[18] J.A. Taylor, E.S. Yeung, J. Chromatogr. 550 (1991) 831.

[19] V. Rohlíček, Z. Deyl, I. Mikšík, J. Chromatogr. A 662 (1994) 369.

[20] M. Macka, P. Andersson, P.R. Haddad, Presented at the International Ion Chromatography Symposium IICS'95, Dallas, TX, 1–5 October 1995, poster No. 94.

[21] M. Macka, P. Zakaria, E.F. Hilder, P. Nesterenko, P.R. Haddad, Presented at the International Ion Chromatography Symposium IICS'98, Osaka, Japan, 28 September–1 October 1998, poster No. 66.

[22] M. Macka, P. Nesterenko, P.R. Haddad, J. Microcol. Sep. 11 (1999) 1.

[23] F.M. Everaerts, J.L. Beckers, T.P.E.M. Verheggen, Isotachophoresis—theory, instrumentation and applications, Journal of Chromatography Library, vol. 6, Elsevier, Amsterdam, 1976, p. 217.

[24] P.Z. Liu, A. Malik, M.C.J. Kuchar, W.P. Vorkink, M.L. Lee, J. Microcol. Sep. 5 (1993) 245.

[25] P.Z. Liu, A. Malik, M.C.J. Kuchar, M.L. Lee, J. Microcol. Sep. 6 (1994) 581.

[26] X. Ren, P.Z. Liu, M.L. Lee, J. Microcol. Sep. 8 (1996) 529.

[27] X. Ren, P.Z. Liu, A. Malik, M.L. Lee, J. Microcol. Sep. 8 (1996) 535.

[28] S. Qui, M.L. Lee, J. Microcol. Sep. 10 (1998) 605.

[29] S.C.C. Chiang, S.F.Y. Li, Biomed. Chromatogr. 11 (1997) 366.

[30] P.J. Schneider, H. Engelhardt, J. Chromatogr. A 802 (1998) 17.

[31] J.F. Rabek, J. Lucki, B. Rånby, Y Watanabe, B.J. Qu, in: J.L. Benham, J.F. Kinstle (Eds.), Chemical Reactions on Polymers, American Chemical Society, Washington, DC, ACS Symposium Series, No. 364, 1988, p. 187.

[32] J.F. McKellar, N.S. Allen, Photochemistry of Man-Made Polymers, Applied Science Publ., London, 1979, p. 11.

[33] T.M. Huang, J. Pawliszyn, Analyst 125 (2000) 1231.

[34] J.I. Kroschwitz, Concise Encyclopedia of Polymer Science and Engineering, Wiley, New York, 1990.

[35] F. Foret, L. Krivánková, P. Bocek, Capillary zone electrophoresis, Electrophoresis Library, VCH, Weinheim, 1993, p. 38.

[36] M. Macka, C. Johns, P. Doble, P.R. Haddad, LC GC 19 (2001) 178.

[37] Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 79th ed., 1998, p. 12-198.

[38] R.H. Perry, D.W. Green, J.O. Maloney (Eds.), Perry's Chemical Engineers' Handbook, McGraw Hill, New York, sixth edition, 1985, p. 3.

[39] M. Macka, P. Andersson, P.R. Haddad, Electrophoresis 17 (1996) 1898.

[40] P.M. Korinek, Macromol. Symp. 82 (1994) 61.

[41] A.V. Kiselev, Ya.I. Yashin, Gas Adsorption Chromatography, Plenum Press, New York, 1969.

[42] V.A. Eroshenko, A.Yu. Fadeev, Ross. Khim. Zhurn. 40 (1994) 92.

[43] M.J. Thornton, J.S. Fritz, J. High Resolut Chromatogr. 20 (1997) 653.

[44] P. Jandik, G. Bonn, Capillary Electrophoresis of Small Molecules and Ions, VCH, New York, 1993.

[45] Q. Liu, F. Lin, R.A. Hartwick, J. Chromatogr. Sci. 36 (1997) 126.

[46] B. Sun, M. Macka, P.R. Haddad, Electrophoresis 23 (2002) 2430.

[47] P. Doble, M. Macka, P. Andersson, P.R. Haddad, Anal. Commun. 34 (1997) 351.

[48] V. Unterholzner, M. Macka, P.R. Haddad, A. Zemann, Analyst 127 (2002) 715.

[49] M. Macka, J. Hutchinson, S. Zhang, A. Zemann, P.R. Haddad, Electrophoresis 24 (2003) 2144.

[50] K.D. Altria, J. Chromatogr. A 892 (2000) 171.

[51] K.D. Altria, J. Cap. Electrophoresis 7 (2002) 11.

[52] S. Terabe, N. Matsubara, Y. Ishihama, Y. Okada, J. Chromatogr. 608 (1992) 23.

[53] A. Landman, P. Sun, R.A. Hartwick, J. Chromatogr. A 669 (1994) 259.

[54] P. Sun, R.A. Hartwick, J. Chromatogr. A 685 (1994) 303.

[55] C. Liu, Y. Ho, Y. Pai, J. Chromatogr. A 879 (2000) 383.

[56] M.A. Rodriguez-Delgado, F.J. Garcia-Montelongo, A. Cifuentes, Anal. Chem. 74 (2002) 257.