Review

Nonaqueous and aqueous capillary electrophoresis of synthetic polymers

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Abstract

In this work, the use of capillary electrophoresis (CE) to analyze synthetic polymers is reviewed including works published till February 2004. The revised works have been classified depending on the CE mode (e.g., free solution capillary electrophoresis, capillary gel electrophoresis, etc.) and type of buffer (i.e., nonaqueous, aqueous and hydro–organic background electrolytes) employed to separate synthetic macromolecules. Advantages and drawbacks of these different separation procedures for polymer analysis are discussed. Also, physicochemical studies of complex polymer systems by CE are reviewed, including drug release studies, synthetic polyampholytes, dendrimers, fullerenes, carbon nanotubes and associative copolymers.
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Contents

1. Introduction

Nowadays, capillary electrophoresis (CE) has become widely used for the separation of biopolymers such as proteins, peptides or DNA fragments as a result of the good possibilities provided by this technique in terms of analysis speed, high efficiency and low sample consumption [1–3]. It is well known that CE allows separation of these substances according to their different molecular size, charge/mass ratio, isoelectric point, etc. Logically, these modes of separation can also be valuable for synthetic polymer characterization [4,5], mainly considering that properties like size and molecular dispersion of synthetic macromolecules have a great influence on their applications. CE has demonstrated to be a very valuable technique for the fast characterization of this kind of polymers. However, since synthetic macromolecules can have a wide variety of forms differing in shape (branched, cross-linked, linear, etc.), sizes (with molecular masses ranging from hundreds to over a million g/mol) and chemical properties (neutral, ionic, hydrophobic, hydrophilic, etc.), no one CE technique is universally applicable to all polymers. In order to deal with this different polymer nature, several CE modes have been used (e.g., free zone capillary electrophoresis, capillary gel electrophoresis, etc.) using nonaqueous, hydro–organic or aqueous separation buffers. Thus, one of the main characteristics of CE is that this technique makes possible the development of uniquely tailored separations, that can monitor very different polymers together with their degradation products or by-products formed during polymerization. Interestingly, such information can be in some cases complementary to that provided by other classical techniques based as size-exclusion chromatography (SEC) or RP-HPLC.

A description of the works that have been published up to now on CE analysis of synthetic polymers is given below.

2. Nonaqueous CE of synthetic polymers

2.1. Polymer analysis by nonaqueous free solution capillary electrophoresis (NAFSCE)

The principal applications of free solution capillary electrophoresis (FSCE) in polymer analysis are: (i) size-based separation of end-charged oligomers with low to moderate degrees of polymerization (DP, typically, $0 < DP < 50$), (ii) separation of evenly charged oligomers of low DP (typically, $DP < 10$), and (iii) separation of copolymers according to their charge density.

The first interest in using nonaqueous FSCE (NAFSCE) for polymer analysis is to increase the solubility of hydrophobic polymers that cannot be analyzed by aqueous or hydro–organic CE. Thus, NAFSCE allows one to extend the range of CE applications to non water-soluble polymers. Of course, the electrophoretic migration is only possible if the polymer solutes are ionized in the background electrolyte (BGE) or in interaction with a charged additive of the separa-

tion medium. Number of non-dissociating solvents currently used in polymer chemistry such as tetrahydrofuran (THF), dichloromethane, chloroform, dioxane, alkanes, etc. have very low dielectric constant (<10) and are usually not considered as potential candidates for performing CE. However, pioneering and more recent studies [6,7] reported the possibility of using non-dissociating solvents as a main component in a BGE for electrophoretic separations. Early work in 1950 [6] reported the possibility to ionize particles (carbon black) in nonconducting solvent such as kerosene or cetane. Electrophoretic mobilities of the particles were very low (in the order of $0.2 \times 10^{-9}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$) but were high enough to be determined and could be increased up to $1.2 \times 10^{-9}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$ in cetane saturated with acetone.

In a recent study, Cottet et al. [7] demonstrated that a high content of non-dissociating solvent can be used as a main component of the electrolyte for polymer analysis. This approach was exemplified by the separation of highly hydrophobic *N*-phenylaniline oligomers, belonging to the family of conductive and electroactive polymers. Electrolytes based on binary solvent mixtures containing a high percentage (e.g., 75%, v/v) of non-dissociating solvents such as chloroform, THF, or dichloromethane and a moderate content of methanol (MeOH) (e.g., 25%, v/v) were used. Electrophoretic migrations of the oligomers were even reported in a THF–MeOH (95:5, v/v) mixture with supporting electrolyte. However, the electrophoretic mobilities were relatively low in this latter case. The ionization (protonation) of the solutes was obtained by the addition of 10 mM perchloric acid in the solvent mixture. The origin of the selectivity was not clearly elucidated but the electrophoretic mobility was a decreasing function of the DP. This observation suggested that the oligomers were not evenly charged since the electrophoretic mobility of evenly charged oligomers is usually an increasing function of the DP for low molecular masses (typically for $DP < 10$, although this limit depends both on the ionic strength of the electrolyte and on the polymer stiffness [8]). The main limitation for using non-dissociating solvents in NACE is their relatively strong UV absorbance (especially chloroform and dichloromethane in the solvents mentioned above).

Methanol and acetonitrile (ACN) are more UV-transparent than aforementioned solvents and, for this reason, they were extensively used in NACE of small molecules (see e.g., [9]). These solvents were also used for polymers or oligomers NAFSCE analysis. Bowser et al. [10] described the separation of porphyrin oligomers based on electrostatic ion–dipole interaction between analytes and a polyether surfactant in a methanolic electrolyte. It was proposed that the polyether complexes with the porphyrins through the carboxylic acid functional groups. These interactions could hardly take place in water-based electrolytes and are favored in methanol due to the low dielectric constant. The methanol-based electrolyte also reduced the aggregation of porphyrin oligomers. Partial separation of 60 peaks was performed in 30 min leading to a qualitative fingerprinting method for characterizing porphyrin samples.