



Separation of linear synthetic polymers in non-aqueous capillary zone electrophoresis using cationic surfactant



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ABSTRACT

A method for separating water-insoluble and neutral synthetic polymers using non-aqueous capillary zone electrophoresis (NACZE) was developed. The non-aqueous solvent system comprising a mixture of tetrahydrofuran, acetonitrile, and ethanol containing cetyltrimethylammonium chloride was used for solubilizing and conferring positive charges to the polymers. A mixture of polystyrene (PS, $M_n = 6500$) and polybutadiene (PBD, $M_n = 5900$) was successfully separated by the NACZE method using cationic surfactants. Evaluation of the effect of the molecular weight of the polymers on the electrophoretic behavior demonstrated that PSs with different molecular weights ($M_n = 6500, 10,200, 19,600, 200,000$) were co-eluted as a single peak. That is, the apparent electrophoretic mobility of the PSs was independent of the molecular weight. In contrast, evaluation of PBD and polycarbonate (PC) demonstrated that the solubility of polymers in the medium affected the apparent electrophoretic mobility of the polymers, where low solubility resulted in reduced apparent electrophoretic mobility. Using the proposed method, poly(styrene-co-methylmethacrylate)s with different compositions were successfully separated.

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1. Introduction

In the field of polymer science, liquid chromatographic methods are often used to characterize linear polymers [1]. The most commonly utilized method is size exclusion chromatography (SEC), with which size-based separation of molecules can be achieved for determining the molecular weight and distribution of polymers [1,2]. Liquid chromatography at critical condition (LCCC) is also used to analyze slight differences in the molecular structure of polymers [1]. LCCC can be used to characterize (or separate) polymers without dependence on the molecular weight; however, optimization of the chromatographic conditions is somewhat time-consuming. HPLC with gradient elution has also been utilized to characterize the polymer composition [1,3]. Temperature rising elution fractionation (TREF) is a technique that is used to characterize the chemical composition of polymers [4].

Capillary electrophoresis (CE) is an alternative separation method that is utilized in various research fields. Electrophoretic methods are frequently used for analysis of biopolymers such as DNAs and proteins [5–9]. However, few studies have focused on electrophoretic separation of synthetic polymers and this technique has been applied to water soluble and charged polymers

[10,11]. Application of CE to the study of synthetic polymers is limited by two main factors. The first is that many synthetic polymers (e.g., polystyrene (PS) and polymethylmethacrylate (PMMA)) are not soluble in aqueous solution, which is generally used as the electrophoretic medium for CE. Secondly, synthetic polymers are often neutral in solution, i.e., no ionizable functional groups are contained in their structure. Therefore, protocols for application of CE to synthetic polymers have not been well developed. However, to address these limitations, we focused on non-aqueous CE (NACE), where non-aqueous solvent has been used as the electrophoretic medium for CE [12–19]. Because linear synthetic polymers are often soluble in organic solvents such as tetrahydrofuran (THF) and chloroform, NACE is a prospective means of resolving the first issue. In non-aqueous capillary zone electrophoresis (NACZE), the separations of charged polymers or polyelectrolytes, such as DNA fragments [20], *N*-phenylaniline oligomers [21], synthetic organic polypeptides [22], angiotensins [18], asphaltene [23], have been reported.

Sodium dodecylsulfate–polyacrylamide gel electrophoresis (SDS–PAGE) is a method for size-based separation of proteins [24]. In SDS–PAGE, anionic SDS interacts with proteins hydrophobically and provides an approximately constant charge/weight ratio (1.4 g SDS for 1 g protein in general). Therefore, in non-aqueous solvent, the charge is conferred to the synthetic polymers and allows electrophoretic migration when suitable ionic surfactants are added to the non-aqueous electrophoretic medium. Li et al. [25] reported

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analyses of synthetic organic, neutral polymers using non-aqueous capillary gel electrophoresis. In this study, stearyltributylphosphonium bromide was used for electrophoretic force to the neutral polymers.

In general, CZE has potentials of both high separation efficiency and different selectivity compared with HPLC separation. Moreover, CZE separation has a potential to be performed with the minimal sample preparation. Therefore, studies of CZE separation of synthetic polymers will contribute the progress in the analyses of synthetic polymers. In this study, the separation of synthetic polymers using NACZE employing ionic surfactants is investigated. Separation of polymers based on their chemical species is achieved, and the effect of the molecular weight on the electrophoretic behavior is also studied. Additionally, the separation of copolymers with different compositions is also demonstrated.

2. Experimental

2.1. Chemicals

Reagents (except for the polymers) were purchased from Wako Pure Chemicals (Osaka, Japan). The organic solvents of THF, acetonitrile (ACN), and ethanol (EtOH) were used as electrophoretic media. SDS and cetyltrimethylammonium chloride (CTAC) were used as surfactants in the non-aqueous solution. Coronene and perylene were used as neutral and highly hydrophobic low molecular weight compounds. Polystyrene (PS, $M_n = 6500, 10,200, 19,600, 200,000$, Showa Denko, Tokyo, Japan except for $M_n = 6500$ (Sowa Science, Tokyo, Japan)), polybutadiene (PBD, $M_n = 5900, 27,000, 280,000$, Sowa Science), polymethylmethacrylate (PMMA, $M_n = 525,000$, Wako), and polycarbonate (PC, $M_n = 6700$) were used as polymer samples. Styrene (St), methylmethacrylate (MMA), and azobisisobutyronitrile (AIBN) were used in the synthesis of poly(styrene-co-methylmethacrylate (St-co-MMA)).

2.2. Synthesis of poly(St-co-MMA)

Random poly(St-co-MMA) copolymers were prepared by the following procedure. A mixture of St, MMA, and AIBN was polymerized in a glass vial for 30 min at 60 °C. At the end of this reaction period, 2 mL of THF was added to the vial and 30 mL of methanol was subsequently added to precipitate the polymer. The product was filtered, and the residue was dried under vacuum. Two types of copolymers were prepared by varying the mixing ratios of St:MMA as 8:2 and 5:5. The molecular weights and the distributions of the copolymers were measured using SEC (LC-20AV system, Shimadzu, Kyoto, Japan) employing GPC-K803 (Showa Denko, Tokyo, Japan) and GPC-K-806M (Showa Denko) columns. The average molecular weight of the polymers prepared using the 8:2 and 5:5 St:MMA ratios were 406,000 ($M_w/M_n = 2.03$) and 645,000 ($M_w/M_n = 1.75$), respectively.

2.3. Apparatus for CE

The commercial instrument, CAPI-3100 (Otsuka electronics, Osaka, Japan) with a fused-silica capillary of i.d. 0.050 mm (effective length 36 cm, whole length 48 cm), was used for CE analysis. Separations were performed by application of +20 kV at 25 °C, and the analytes were detected by monitoring the UV absorbance at 212 nm. The capillary was sequentially washed with THF (180 s), EtOH (180 s), and electrophoretic medium (180 s) before each run. The sample solution was injected by a hydrodynamic method ($\Delta H = 25$ mm, 30 s). The organic solvents did not damaged to the apparatus, because the organic solvents were contact only with a

Table 1

Solubility (in mM) of ionic surfactants in non-aqueous solvents at room temperature.

Surfactant	THF	ACN	EtOH
SDS	<1	5	<100
CTAC	<1	60	>700

fused-silica capillary, platinum electrodes, and glass vials in CAPI-3100.

2.4. HPLC with gradient elution

For characterization of the polymers, HPLC with gradient elution was performed using a Shimadzu LC-10A system (Shimadzu) with an ODS column (Chemcobond 5-ODS-H, Chemco-Puls, Osaka, Japan) at 40 °C. The mobile phase composition was altered from ACN/THF (90/10) to ACN/THF (0/100) in the gradient elution at a flow rate of 1.0 mL/min.

3. Results and discussion

3.1. Non-aqueous solvent containing ionic surfactant

In the initial evaluation of non-aqueous solvents containing ionic surfactants as the CE media, the mixtures containing THF and ACN were selected as the base medium for electrophoresis because THF and ACN are respectively good and poor solvents for the linear synthetic polymers used in this study. ACN was used to control the hydrophobic interaction between the ionic surfactants and polymers because the polarity of ACN is relatively higher than that of THF. The solubilities of SDS and CTAC in THF and ACN at room temperature were measured. As shown in Table 1, THF was a poor solvent for both ionic surfactants, and the solubilities in ACN were also low. Because the concentration of the surfactant is an important factor for controlling the electrophoretic behavior, an additional organic solvent would be necessary to enhance the solubility of the surfactant. As clearly indicated in Table 1, ethanol was a good solvent for CTAC as well as SDS. Since the solubility of CTAC in the solvents was superior to that of SDS, CTAC was used as the additive in this study. On this basis, a mixture of THF, ACN, and EtOH containing CTAC was used as the electrophoretic medium.

The four mixtures of THF/ACN/EtOH (10/89/1, 10/88/2, 10/85/5, and 10/83/7 in volumetric ratio) were evaluated as the electrophoretic medium. With the mixture containing 1% EtOH, the addition of 10 mM CTAC resulted in unstable baseline. Both the mixtures containing 2% and 5% EtOH provided stable baseline with the addition of 10 mM CTAC whereas it became unstable with the addition of 30 mM CATC. In the case 7% EtOH, a stable baseline was kept until the addition of 50 mM CTAC. Therefore, the volumetric ratio of EtOH in the mixture was kept at 7% (v/v) to ensure solubility of CTAC in the mixture.

3.2. Separation of low molecular weight hydrophobic neutral compounds

For the basic study of NACZE using ionic surfactants, the electrophoretic behavior of hydrophobic neutral compounds was investigated using the mixture of THF/ACN/EtOH (10/83/7). Fig. 1 shows the separation of coronene and perylene using NACZE with different CTAC concentrations. When the CTAC concentration was low (A, 10 mM), coronene and perylene were not separated. Increasing the CTAC concentration reduced elution of the analytes and enhanced the resolution as shown in Fig. 1B and C. As shown in Fig. 1, the CTA cations successfully conferred positive charge to the neutral compounds in NACZE. In Fig. 1, coronene was detected prior to perylene. Because the positive voltage was applied to the inlet

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