Migration Behavior of the Polymer Particles Possessing Carboxylate and Borate Moieties in Capillary Electrophoresis

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Migration behavior of functional polymer particles, such as carboxylic acid- and phenylboric acid-modified polymer particles, was examined in capillary electrophoresis (CE) using migration buffers containing metal ions or saccharides. It was found that the interaction between functional groups on the particles and the specific chemical species in the migration buffers influenced the migration behavior of the polymer particles. The obtained results supported the possibility that CE becomes useful method for examining the property of functional polymer particles.

Functional polymer particles and their aqueous dispersion have become of interest in various fields including analytical chemistry. The polymer particles of sub-micron diameter are characterized by large surface area, comparable with porous glass beads, and show high reactivity near the surface. Ide et al. synthesized water-insoluble polyacrylamide particles and examined its application to adsorption of metal ions.[1] We also examined adsorption of metal ions onto carboxylic acid-modified polymer particles synthesized by seeded emulsion polymerization.[2] Instrumental analyses (IR, NMR, ESR, SEM, etc.) as well as such an adsorption equilibrium test have given useful information to studies concerning the functional polymer particles.[3]

On the other hand, capillary electrophoresis (CE) has been shown to be a powerful and efficient analytical technique.[4] Jones et al. achieved separation of chemically different polymer particles by CE.[5] Here, we proposed to use CE for examining functional polymer particles. Migration times of carboxylic acid- and phenylboric acid-modified polymer particles were examined; interesting behavior was observed in the migration buffers containing metal ions or saccharides.

All of the reagents used were of commercially available special grade. Ion-exchanged water was distilled for use. Carboxylic acid-modified polymer particles (CAR-P) (0.53-μm average diameter and 2.2×10^{-4} mol-carboxy group on the surface per g-particle) were prepared from divinylbenzene, styrene, butyl acrylate, and methacrylic acid.[1] The two types of phenylboric acid-modified polymer particles were synthesized from styrene, butyl acrylate, and *m*-acrylamidophenylboronic acid through two different steps, without or with methyl ethyl ketone (MEK) treatment.[6] They are called here PEN-P and PEN-P-MEK, respectively. PEN-P-MEK possessed much more phenylboric acid groups on the surface than did PEN-P. PEN-P-MEK featured 0.51-μm average diameter and 1.5×10^{-5} mol-phenylboric acid groups on the surface per g-particle. The characterization of CAR-P, PEN-P, and PEN-P-MEK had been carried out in detail in the previous papers.[1,3,6]

A fused-silica capillary (50-μm i. d., 50-cm length (effective length of 30 cm)) was treated with 1 mol dm^{-3} sodium hydroxide for 30 min and washed with distilled water. The capillary was filled with a migration buffer in advance and an aliquot of emulsion of polymer particles was introduced as a sample into the capillary for 15 s from 25 cm height by siphoning. Applied voltage of 15 kV was used and the particles were migrated and detected with a modified spectrophotometric detector of Shimadzu Co. SPD-6AV (254 nm).

Migration times of CAR-P (2.4 g dm^{-3}) were examined by use of a migration buffer (10 mmol dm^{-3} phthalate buffer; pH 5.5) containing transition metal ions (Cu(II), Ni(II), or Co(II)) and rare earth metal ions (Lu(III), Eu(III), or La(III)) (Table 1). Each concentration of metal ion was 2.6 mmol dm^{-3}. The electropherogram in the absence of metal ions is shown in Figure 1; the peak of CAR-P was observed at ca. 7.2 min. The shapes of CAR-P peaks were almost the same both in the absence and presence of metal ions. The migration times were shortened with Cu(II), Ni(II), and Co(II) as well as Lu(III), Eu(III), and La(III) in these orders. The orders corresponded to those of the Irving–Williams series and their metal ion radii. That is, the larger the interaction between the particles and the metal ions, the faster the migration times. The amounts of carboxylate anions on the polymer surface decreased through the interaction with the metal ions. The interaction lowered an electrophoretic mobility toward the capillary inlet (anodic electrode). Consequently, the migration times of the polymer particles decreased with increasing the interaction between the particles and the metal ions.

Table 1. Migration times of CAR-P in the migration buffer containing metal ion

Metal ion	Migration time / min
Cu(II)	5.58
Ni(II)	6.31
Co(II)	7.08
Lu(III)	6.01
Eu(III)	6.46
La(III)	6.98

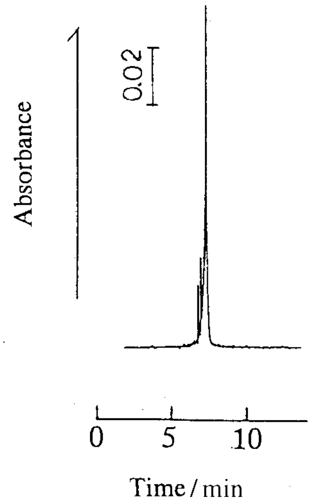

Figure 1. Electropherogram of CAR-P in the absence of metal ions.

Electrophoretic behavior of phenylboric acid-modified polymer particles (1.3 g dm^{-3}) was also examined. The signal of PEN-P-MEK appeared with almost the same electropherogram as shown in Figure 1, while that of PEN-P never appeared within 1 h in various migration buffers (10 mmol dm^{-3} carbonate buffer; pH 8.0, 9.0, 10.0, and 11.0). The exact reason is not known. However, the phenylboric acid moiety become anion type in an alkaline solution, and the negative charge must play an important role in migration of the polymer particles. PEN-P which had less negative charge than PEN-P-MEK may aggregate in the capillary and have some interaction with an inner wall of capillary, leading to no-appearance of the signal.

Figure 2 shows the effect of D-glucose and 1-methyl-α-D-glucoside containing in the migration buffers on the migration times of PEN-P-MEK. The saccharide concentration used was 6.4 mmol dm^{-3}. It is known that phenylboric acid forms a five-membered ring with a *cis*-1,2-diol group. Phenylboric acid reacts with diol group in an alkaline solution through tetrahedral structure of boron having hydroxide anion. In addition, it can form a six-membered ring with a *trans*-CH(OH)–CH(CH_2OH)-diol group although the stability is inferior to that of the five-membered ring.[7,8] D-Glucose has a *cis*-1,2-diol group and a *trans*-CH(OH)–CH(CH_2OH)-diol group. 1-Methyl-α-D-glucoside has only a *trans*-CH(OH)–CH(CH_2OH)-diol group. Therefore, D-glucose possesses stronger affinity to phenylboric acid moiety on the polymer particles than did 1-methyl-α-D-glucoside. As shown in Figure 2, the migration times increased with no-saccharide, 1-methyl-α-D-glucoside, and D-glucose in this order. Phenylboric acid reacts with diol group in an alkaline solution through tetrahedral structure of boron having hydroxide anion. That is, the migration times delayed probably because the negative charge was more effectively formed due to the coordination of hydroxide anion to phenylboric acid moiety when binding with saccharide molecules.

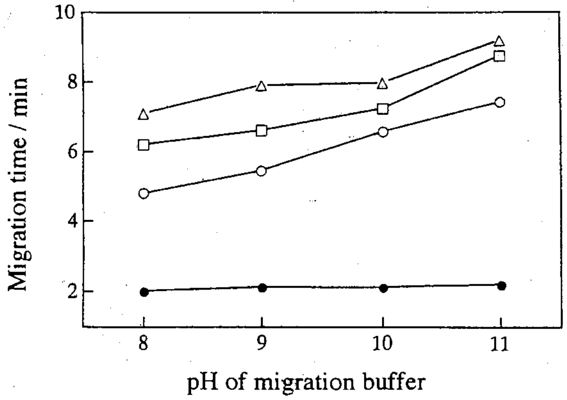

Figure 2. The effect of saccharide contained in the migration solutions on the migration times of PEN-P-MEK. ●, Acetone (neutral marker); ○, no-saccharide; □, 1-methyl-α-D-glucoside; and △, D-glucose.

The electrophoretic behavior of the polymer particles reflected the interaction between the functional groups on the particles and the specific chemical species containing in the migration buffers. By use of such behaviors of polymer particles, the mixture of sevral kinds of polymer particles may be separated in the capillary electrophoresis due to their characteristic. Although the obtained data here were somewhat qualitative, they no doubt clarified that CE is one of available instrumental analyses to examine the property of functional polymer particles.

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