

Ionic liquids enable accurate chromatographic analysis of polyelectrolytes

メタデータ	言語: English 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: Kuroda, Kosuke, Ohno, Hiroyuki, 黒田, 浩介 メールアドレス: 所属:
URL	https://doi.org/10.24517/00009617

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Electronic Supplemental Information

Ionic liquids enable accurate chromatographic analysis of polyelectrolytes

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Materials and Methods

Materials

1-Ethyl-3-methylimidazolium methylphosphonate ($[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$) was synthesized as previous literature. Sodium polystylenesulfonate (PSS; Sowa Kagaku corporation) and Polyallylamine (PAA; Sigma-aldrich) was purchased and used without further pretreatment. Polystylenesulfonic acid was synthesized from sodium polystylenesulfonate (M_w : 7k) mentioned above by using ion-exchange resin (Amberlite-IRN77, from Sigma-aldrich). Diallyldimethylammonium salt/maleic acid copolymer was provided from Nittobo Medical Co., Ltd. and used as received.

HPILC measurement

Components in the HPLC system used were high pressure durable pump (LC-20AD; Shimadzu), an injector (7725; Rheodyne) with a 5 μL loop, and a refractive index detector (Shodex RI-71; Showa Denko). Columns filled with silica gel [Shodex KW-402.5-4F, 4.6 mm (inner diameter) \times 300 mm, and KW-405-4B, 4.6 mm (inner diameter) \times 50 mm; Showa Denko] were used in tandem. The columns were heated at 55 $^\circ\text{C}$ using a column oven

(CTO-10Avp; Shimadzu). The RI detector cells were maintained at 40 °C. The flow rate was set at 0.01 mL min⁻¹. For data acquisition and processing we used the software package SIC-480 II XP (SIC). [C₂mim][(MeO)(H)PO₂] was used as an eluent under an helium atmosphere.

Synthesis of [C₂mim][(MeO)(H)PO₂]

Reaction scheme was shown in Scheme S1. 1-Ethylimidazole (100g, 1.04 mol) and dimethyl phosphite (126g, 1.14 mol) were slowly mixed under an argon gas atmosphere at room temperature without solvent. The reaction mixture was stirred at 80 °C for 24h. The resulting liquid was washed repeatedly with excess dehydrated diethyl ether. The residual liquid was dissolved in dichloromethane, and the resulting solution was passed through a column filled with neutral activated alumina. After removal of dichloromethane, the residual liquid was dried *in vacuo* at 80 °C for 24h to give [C₂mim][(MeO)(H)PO₂] as a colourless liquid. The yield was about 80%.

Structure of [C₂mim][(MeO)(H)PO₂] was confirmed by ¹H- and ¹³C-NMR spectra (JEOL ECX-400). ¹H-NMR δ_H (400 MHz; CDCl₃; Me₄Si); 1.58 (3H, t, *J* = 7.3 Hz, NCH₂CH₃), 3.55 (3H, d, *J* = 11.9 Hz, POCH₃), 4.06 (3H, s, NCH₃), 4.36 (2H, q, *J* = 7.3 Hz, NCH₂CH₃), 6.92 (1H, d, *J* = 588.5 Hz, PH), 7.58 (2H, d, *J* = 11.3 Hz, NCHCHN), 10.66 (1H, s, NCHN). ¹³C-NMR δ_c (400 MHz; CDCl₃; Me₄Si); 15.22 (NCH₂CH₃), 35.87 (NCH₃), 44.98 (NCH₂CH₃), 50.05 (POCH₃), 121.35 (NCHCHN), 123.17 (NCHCHN), 138.40 (NCHN). ESI-TOF-MS: calcd for C₇H₁₅N₂O₃P [M]⁺: m/z = 111.17; found: 111.37.



Scheme S1 Synthetic scheme of [C₂mim][(MeO)(H)PO₂].

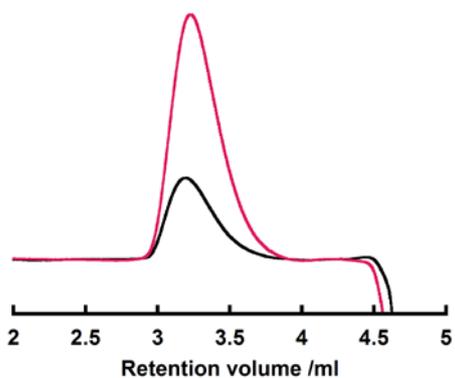


Fig. S1 Chromatograms of NaPSS.

Load amount: 0.5 mg (black) or 2.0 mg (pink) of NaPSS was dissolved in 200 mg of ILs.

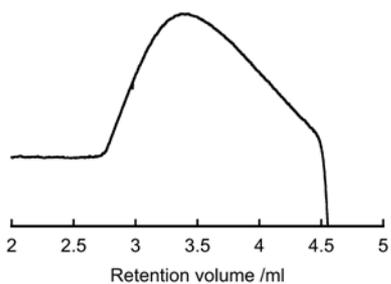


Fig. S2 Chromatogram of diallyldimethylammonium salt/maleic acid copolymer

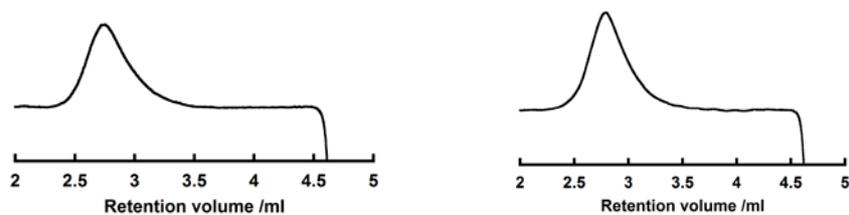


Fig. S3 Chromatograms of gelatin (left), and silk (right).

As seen in Fig. S1, there is no polymer concentration effect on the HPILC peak. Also, the HPILC technique was applied to polyampholytes (Fig. S2). Diallyldimethylammonium salt/maleic acid copolymer was used as a polyampholyte sample. Broader chromatogram was found in this case reflecting large molecular weight distribution. The sample was strongly suggested to contain small molecular weight oligomers and even monomers. For the samples of charged proteins, gelatin and silk were examined with the HPILC as seen in Fig. S3. These data strongly show that the HPILC is a powerful tool to evaluate molecular weight distribution of charged polymers regardless of charge species and charge density.