CHEMISTRY LETTERS, pp. 403-406, 1994.

Poly(sulfonium cation) for Synthesis of High Molecular Weight Poly(phenylene sulfide)

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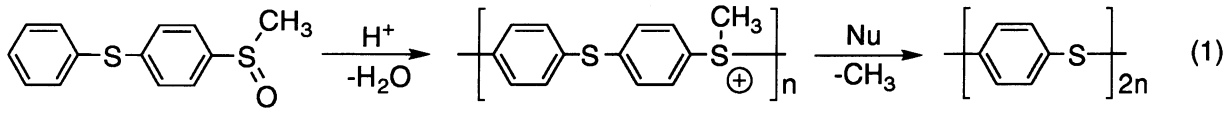
Solution viscosity of Poly(methyl 4-phenylthiophenylsulfonium trifluoromethanesulfonate) as a novel polycation was measured in aqueous acetonitrile solution and formic acid. In the presence of sodium trifluoromethanesulfonate as supporting electrolyte, K and α values are determined to be $K = 7.46 \times 10^{-7}$ and $\alpha = 1.30$ of Mark - Houwink equation in formic acid, in which the molecular weight of the poly(sulfonium cation) is estimated from that of poly(phenylene sulfide).

Poly(arylene sulfide)(PAS) has been deserved much attention as a high performance excellent engineering plastic possessing good thermal stability and chemical resistance.[1-4] These physico-chemical properties are influenced strongly of its molecular weight. Until now, much effort has been consumed on the formation of high molecular weight PAS and also the determination of the molecular weight which is mainly measured by high temperature GPC. Recently, new synthetic route to make a high molecular weight poly(phenylene sulfide)(PPS) via poly(methyl 4-phenylthiophenylsulfonium trifluoromethanesulfonate) [poly(sulfonium cation)] has been reported (Eq. 1).[5,6]



(1)

The poly(sulfonium cation) is soluble in common solvents such as acetonitrile, DMSO, formic acid and sulfuric acid. However, PPS has poor solubility in various solvents, which not only make it difficult to synthesize under mild conditions but also to characterize, e.g., determination of molecular weight. In this paper, the viscosity of poly(sulfonium cation) as a novel polyelectrolyte which is a useful precursor

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of PPS synthesis was determined in acetonitrile solution (50 vol% aqueous) and in formic acid.

The poly(sulfonium cation) containing trifluoromethanesulfonate as counter anion was synthesized by polymerization of methyl 4-phenylthiophenyl sulfoxide in trifluoromethanesulfonic acid as a strong acid. Poly(sulfonium cation)s with different molecular weight are obtained by controlling the polymerization time and concentration. Typical polymerization procedure is as follows. A three necked 200 mL round-bottom flask with a Teflon-covered mechanical stirring stick, a dropping funnel and a thermometer was charged with methyl 4-phenylthiophenyl sulfoxide (5 g, 20.2 mmol). The reaction mixture was cooled to 0 °C. To the mixture trifluoromethanesulfonic acid (25 mL) was added and stirred. The trifluoromethanesulfonic acid acts both as a solvent of the polymerization and a reagent for protonation to the sulfoxide. After 10 min mixing, the reaction mixture was allowed to warm to room temperature. The reaction mixture turned to pale blue. Stirring was continued for 20 h at room temperature. Thereafter the reaction mixture was poured into ice water (1 L), the precipitate was collected and washed by water. The resulting polymer was chopped in a blender, washed with water and dried in vacuum at room temperature over P_2O_5 for 20 h. Yield is 7.63 g (100%).[7] PPS can be obtained by a nucleophilic demethylation of the poly(sulfonium cation).[8] PPSs with Mw = 11400, 20100, 28300, 39100, 70100, 95200 were prepared by the method (Fig.1).

The poly(sulfonium cation) with trifluoromethanesulfonate anion is a new type polyelectrolyte which has alternative structure of positively charged phenylsulfonium and phenylsulfide. The solution viscosity and solubility of a polyelectrolyte are influenced by a co-existence of supporting electrolyte and solvent species. The poly(sulfonium cation) is insoluble in aqueous solution but soluble in polar organic solvent, e.g. acetone, acetonitrile and dimethyl sulfoxide (DMSO). In particular, the polycation is soluble in acetonitrile and formic acid more easily (solubility : more than 100 mg / mL). The viscosity measurement was performed using an Ubbelohde viscometer in the presence of sodium trifluoromethanesulfonate as supporting electrolyte.[9] In the absence of the supporting electrolyte, the viscosity curve in acetonitrile shows a typical polycation characteristic. In the region of the dilute concentration, the viscosity was increased drastically. The viscosity in dilute concentration also increased by additional water since the ionic dissociation is promoted by the addition of water. The solubility in acetonitrile is based on a strong hydrophobic property of the phenylthio group. The ionic dissociation in the presence of water comes from a strong hydrophilicity of the positively charged phenylsulfonium group. Since the hydrophobicity of the polycation is believed to be stronger than hydrohilicity, the polycation in acetonitrile/water =50/50(vol%/vol%) shows the highest viscosity in the absence of the supporting electrolyte (the polycation is insoluble in acetonitrile with > 70% water). In the presence of the supporting electrolyte (50 mM), the

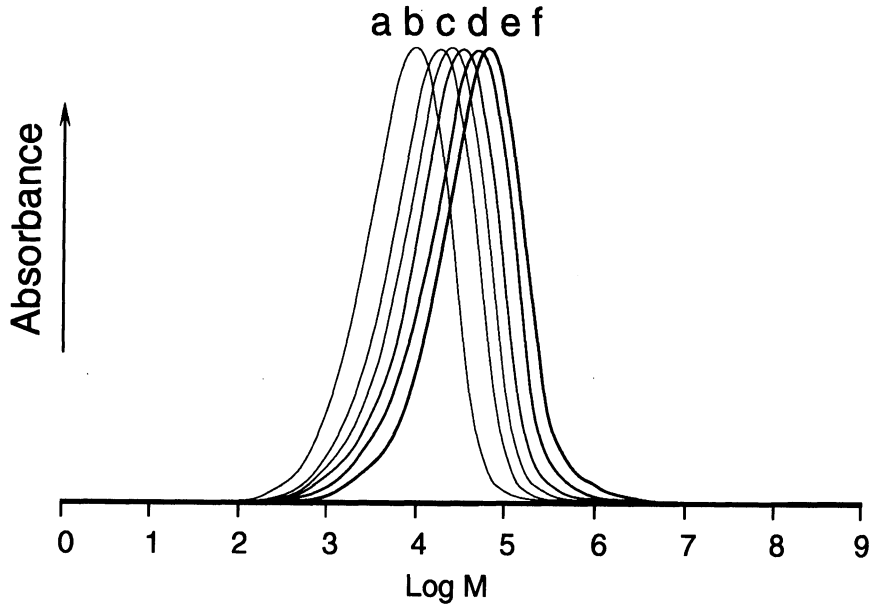

Fig.1. GPC elution curves of the PPS with UV detector (360 nm, eluent : α-chloronaphtalene, 1 mL/min, 210 °C) for determination of molecular weight. 11400(MWD:3.1)(a), 20100(MWD:3.3) (b), 28300 (MWD:3.5)(c), 39100 (MWD:3.7) (d), 70100 (MWD:4.0) (e), 95200(MWD:4.2) (f).

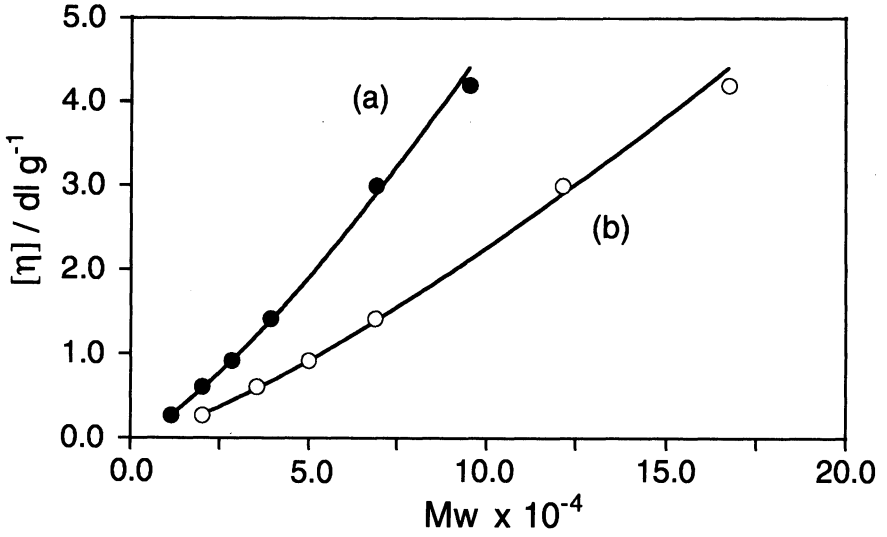

Fig.2. Relationship between viscosity of Poly(sulfonium cation) and molecular weight of PPS (after demethylated)(●) , and between viscosity of Poly(sulfonium cation) and molecular weight of poly(sulfonium cation)(○) .Viscosity was determined in formic acid containing sodium trifluoromethanesulfonate(50 mM, 23 °C).

viscosity curve becomes linear like a non-polyelectrolyte. Limiting viscosity of poly(sulfonium cation)s with various molecular weight were correlated to the molecular weight of the demethylated PPS(Fig.2). The curve is fitted with good agreement as a function : $y=ax^b$. In the relation between the viscosity of the polycation and the molecular weight of PPS, K and α values of Mark - Houwink equation, $[\eta] = K M^{\alpha}$,

were determined to be 1.55 x 10^{-6} and 1.30 respectively. From relation between viscosity of polycation and M-cation which was estimated by an equation $M_{cation} = M(C_{14}H_{11}S_3F_3O_3)/ M(C_{12}H_8S_2) \times M_{pps}$ (M : molecular weight), K and α were determined to be 7.46 x 10^{-7} and 1.30 respectively. This work was partially supported by a Grant-in-Aid for Development Scientific Research No. 04555223 and Scientific Research No.05650865 from the Ministry of Education , Science and Culture, Japan.

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7) IR (KBr, cm^{-1}) 3086, 3023, 2932, 1570, 1478, 1422, 1258, 638, 1161, 1066, 816; ^{1}H-NMR(CD_3CN, 400MHz) δ 7.63, 7.66, 7.85, 7.88 (AB quartet, phenyl 8H), 3.60 (s, methyl 3H). ^{13}C-NMR(CD3CN, 400 MHz) δ 126.2, 132.2, 133.8, 143.0 (phenyl C), 29.0 (methyl C). Anal. Found:C,44.29 ;H, 2.83%. Calcd for $C_{14}H_{11}S_3F_3O_3$: C,44.20 ; H, 2.91%.

8) Poly(sulfonium cation)(1 g) was demethylated by S_N2 nucleophilic reaction with pyridine(10 mL) in acetonitrile(10 mL) for 20 h. The procedure of the demethylation has been described in ref 6. Poly(phenylene sulfide): IR (KBr, cm^{-1}) 3065, 1572, 1472, 1387, 1091, 1074, 1009, 810, 554, 480; CP/MAS ^{13}C-NMR(100MHz) δ 132.1, 134.5 (phenyl C). Anal. Found: C, 66.59; H, 3.83%. Calcd for C_6H_4S: C, 66.63 ;H, 3.73%.

9) CF_3SO_3Na (905 mg, 5.26 mmol) was dissolved in acetonitrile / waster = 50/50 (vol% / vol%) 100 mL as solution A. Poly(sulfonium cation) 200 mg was dissolved in the solution 10 mL and was added into an Ubbelohde viscometer. For all measurement of the viscosity at 25 °C, the solution was diluted to half concentration with solution A. On the basis of the correlation plot of c(g dl^{-1}, concentration of polycation) and η_{sp} (specific viscosity)/c, limiting viscosity number [η] can be obtained from the intersection of vertical axis.

(Received October 14, 1993)