Electronic Supplementary Information for

Lipophilic Polyelectrolyte Gel Derived from Phosphonium Borate Can Absorb Wide Range of Organic Solvents

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Electronic Supplementary Information for

Experimental section

Materials and measurements

All solvents and chemicals are commercially available, and used without purification unless otherwise noted. Styrene and divinylbenzene were purified through silica. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (**NaTFPB**) was synthesized according to the reported methods.[1] The lipophilic monomer and polyelectrolyte gel from alkylammonium salt were prepared as previously reported.[2] ^{1}H NMR spectra were measured on a Bruker DRX500, using 0.05% tetramethylsilane (TMS) as an internal standard. Mass spectral data were obtained using Bruker Autoflex Speed. X-ray photoelectron spectroscopy was carried out on JPS-9200 (JEOL Ltd.) using MgKα X-ray source.

Synthesis of 4-vinylbenzyltriphenylphosphonium chloride (2)[3]

In a 50 mL flask, 4-(chloromethyl)styrene(0.89 g, 5.83 mmol) was added dropwise to a stirred solution of triphenylphosphine (1.52 g, 5.80 mmol) in acetonitrile (10 mL). The homogeneous solution was stirred at 50°C for 24 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and washed by stirring with excess amount of acetone. The precipitate was finally washed with diethyl ether and dried under vaccum to afford **2** as white solid (1.72 g, 78%).

^{1}H NMR (500MHz DMSO-d_6, TMS standard, r.t.): δ 7.91-7.81 (m, 3H, Ph*H*), 7.77-7.73 (m, 6H, Ph*H*), 7.69-7.66 (m, 6H, Ph*H*), 7.34 (d, *J*=8.0 Hz, 2H, Ph*H*), 6.93 (d, *J*=6.0 Hz, 2H, Ph*H*), 6.66 (dd, *J*=11.0,

17.6 Hz, 1H, alkene*H*), 5.82 (d, *J*=17.8 Hz, 1H, alkene*H*), 5.27 (d, *J*=10.8, 1H, alkene*H*), 5.17 (s, 1H, P*CH*$_2$Ph), 5.14 (s, 1H, P*CH*$_2$Ph). MS (MALDI-TOF): m/z calcd. for $C_{27}H_{24}P^+$: 379.16; found: 379.31.

Synthesis of 4-vinylbenzyltriphenylphosphonium TFPB (1)

Compound **2** (1.02 g, 2.45 mmol) and **NaTFPB** (2.15 g, 2.42 mmol) were dissolved in methanol (10 mL) and stirred at room temperature for 18 h. After removal of the solvent, the precipitate was dissolved in dichloromethane and washed with water. The organic layer was separated and dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatograph (silica gel, hexane/acetone = 2/1 (v/v)) to afford **1** as slightly yellow solid (2.39 g, 82%). ^{1}H NMR (500MHz $CDCl_3$, TMS standard, r.t.): δ 7.80-7.77 (m, 3H, Ph*H*), 7.70 (s, 8H, Ph*H*), 7.61-7.57 (m, 6H, Ph*H*), 7.49 (s, 4H, Ph*H*), 7.38-7.33 (m, 6H, Ph*H*), 7.27 (m, 2H, Ph*H*), 6.73 (d, *J*=8.0 Hz, 2H, Ph*H*), 6.63 (dd, *J*=10.9, 17.6 Hz, 1H, alkene*H*), 5.75 (d, *J*=17.6 Hz, 1H, alkene*H*), 5.33 (d, *J*=10.9, 1H, alkene*H*), 5.17 (s, 1H, P*CH*$_2$Ph), 5.14 (s, 1H, P*CH*$_2$Ph).

Preparation of a linear polymer

The ionic monomer **1** (186 mg, 0.15 mmol), styrene (297 mg, 2.85 mmol), and AIBN (4.9 mg 30 μmol) were placed in a glass tube and dissolved in THF 300 μL. The solution was degassed by five

freeze/thaw cycle and polymerized by heating at 65 °C for 24 hours. The feed ratio was adjusted to **1**:styrene = 5:95. The polymer was purified by dialysis in acetone to remove unreacted monomer.

Preparation of gels

Gelation conditions are summarized in Table S1. A typical protocol is as follows; The ionic monomer **1 (**311 mg 、 0.25 mmol), styrene (495 mg, 4.75 mmol), divinylbemzene (DVB) (6.52 mg, 0.05 mmol), and AIBN (8.21 mg, 0.05 mmol) were placed in a glass tube and dissolved in THF 500 μl. The solution was degassed by three freeze/thaw cycle and polymerized by heating at 65°C for 24 hours. The feed ratio was adjusted to **1**: styrene: **DVB** = 5:95:1. As a reference, non ionic gel (**NG**) was prepared under the same copolymerization condition (styrene: DVB = 100: 1) without **1**. The formed gels, **EG** and **NG** were washed by swelling in THF, and air-dried at room temperature, then the samples were dried in *vacuo* at 45 °C.

Table S1. Preparation of **EG-P**, **EG-N**, and **NG**.

Entry	Ionic monomer (mol/L)	Styrene (mol/L)	DVB (mol/L)	AIBN (mol/L)
EG-P	0.5	9.5	0.1	0.1
EG-N	0.5	9.5	0.1	0.1
NG	0	10	0.1	0.1

Conversion of EG-P to NG-PM by Wittig reaction

EG-P (50 mg, reactive site: 2.4 μmol) was swelled by immersed in DMF for 24 hours under N_2. After swelling, propionaldehyde (2.1 mg, 36 μmol) was added to the gel. The addition of DMF solution of *t*-BuOK (4.0 mg, 36 μmol) led to the appearance of orange coloration that disappeared within a few hours. To complete the reaction, these process that added reactants were repeated three cycle. The reacted gel, **NG-PM** was washed by swelling in DMF and air-dried at room temperature, then the samples were dried in *vacuo* at 45 °C.

Measurement of swelling degree (*Q*)

A sliced gel was placed in the following typical organic solvents with various polarities at room temperature. [4]; toluene (dielectric constant ε= 2.4), chloroform (ε = 4.8), Tetrahydropyrane (ε = 5.6) ethyl acetate (AcOEt) (ε = 6.0), tetrahydrofuran (THF) (ε = 7.6), dichloromethane (ε = 8.9), 1,2-dichloroethane (ε = 10.4), 2-octanone (ε = 10.4), 1-hexanol (ε = 13.3), acetone (ε = 20.6), ethanol (EtOH) (ε = 24.6), *N*-methyl-2-pyrrolidone (NMP) (ε = 32.2), methanol (MeOH) (ε = 32.7), *N,N*-dimethylformamide (DMF) (ε = 37.0), and dimethylsulfoxide (DMSO) (ε = 47.0). After immersion for 2 days, we measured the swelling degrees (Q) of the gels defined as the following equation; $Q = (W_{wet}-W_{dry}) / W_{dry}$ (*wt* / *wt*) where W_{dry} and W_{wet} are weights of the dried gel and the wet gel, respectively. The Q indicates the weight ratio of the amount of the solvent entrapped in the gel over that of the dried gel

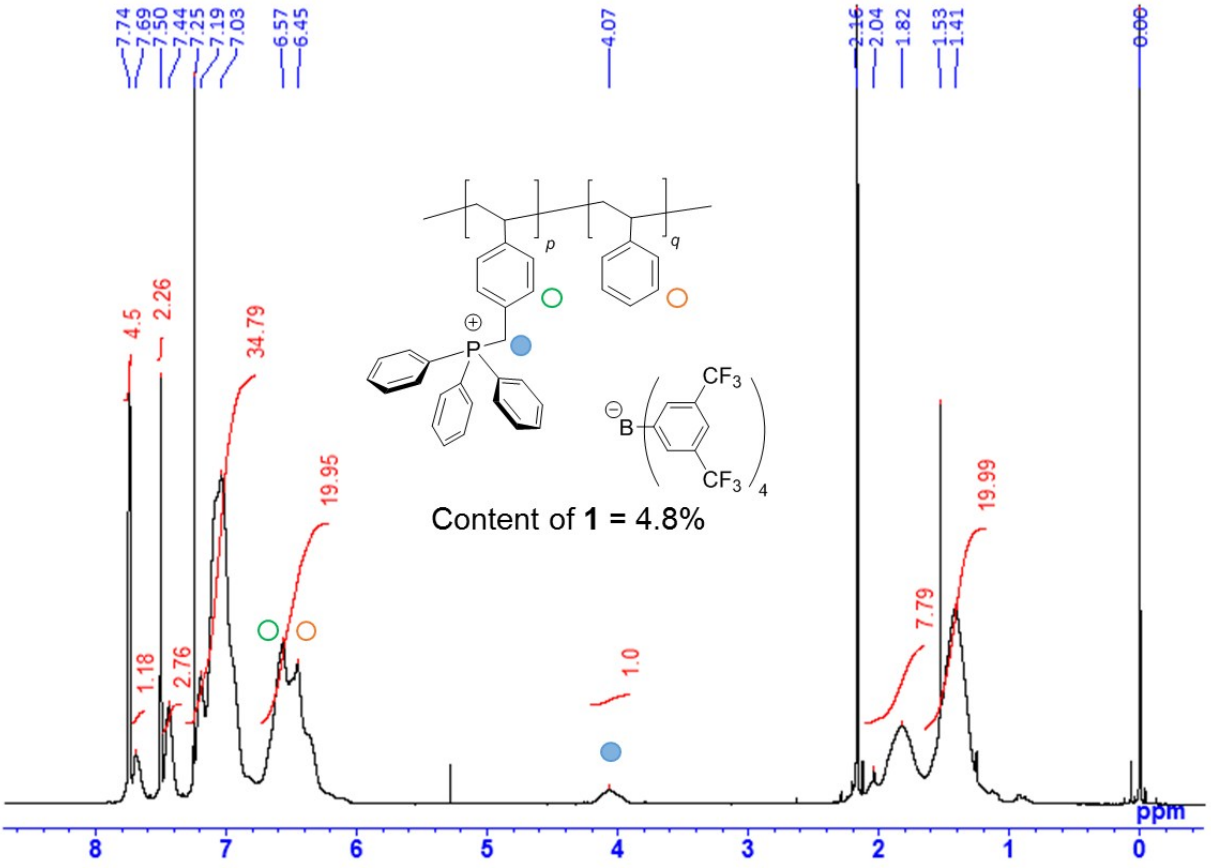

Fig. S1 ^{1}H NMR spectrum of **PS-P**; The copolymerization rate of the ionic site found to be 4.8% according to integration of ionic monomer and styrene.

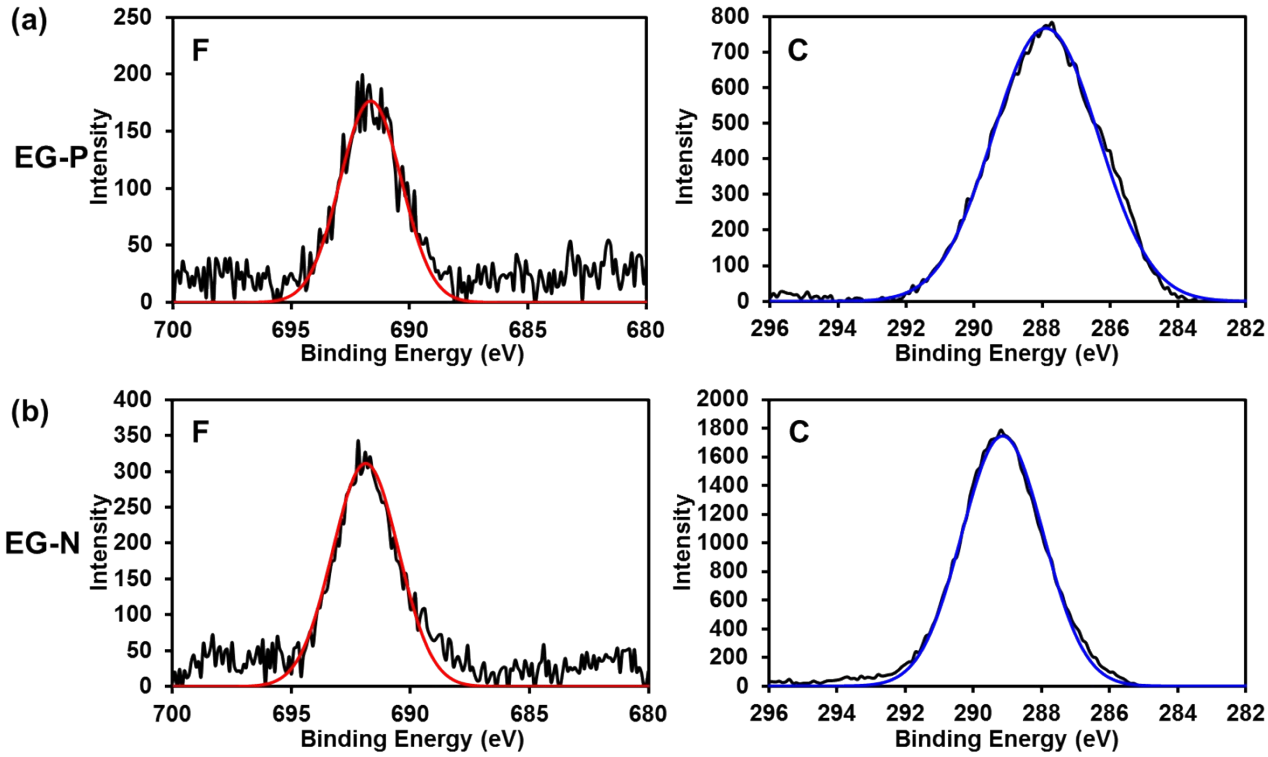

Fig. S2 XPS spectra of (a) **EG-P** and (b) **EG-N** for F and C region.

Table S2. Results of elemental analysis for **EG-P**, **EG-N**, and **NG-PM**.

Sample		C(%)	H(%)	F(%)
EG-P	Calcd.	78.81	6.06	13.85
	Found	77.74	5.80	14.35
EG-N	Calcd.	78.69	6.72	13.82
	Found	77.81	6.59	14.69
NG-PM	Calcd.	91.96	8.03	0.00
	Found	90.05	7.77	N.D.[a]

[a] Not detected (under 1.00%).

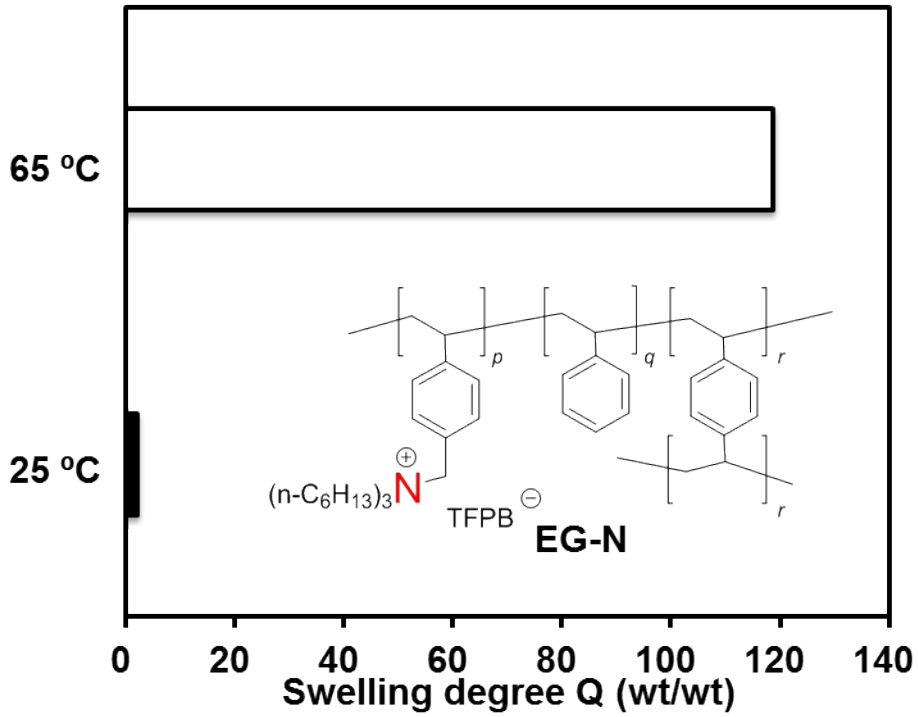

Fig. S3 Swelling degrees of **EG-N** in DMSO at 25 °C and 65 °C.

References

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3. Y. P. Borgueta, N. V. Tsarevsky, *Polym. Chem.*, 2012, **3**, 2487–2494.