

## High Swelling Ability of Polystyrene-Based Polyelectrolyte Gels at Low Temperature

Kazuya Iseda, Masahiko Ohta, Toshikazu Ono and Kazuki Sada\*

Department of Chemistry,  
Graduate School of Science, Hokkaido University,  
Kita 10, Nishi 8, Kita, Sapporo, 060-0810, Japan.

[sadatcm@mail.sci.hokudai.ac.jp](mailto:sadatcm@mail.sci.hokudai.ac.jp)

### Contents:

1. General	p. 2
2. Preparation of ionic monomers and gels	p. 3
3. Measurement of Swelling Degrees	p. 5
Reference	p. 5

## 1. General

Tri-(*n*-hexyl)amine, 4-(chloromethyl)styrene, azobisisobutyronitrile (AIBN), styrene and divinylbenzene were purchased from Tokyo Chemical Ind. Co. Styrene was purified by distillation before used. All solvents were purchased from some commercial suppliers and were used without further purification. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (**NaTFPB**) was synthesized according to the reported methods.<sup>1</sup> Compound **1** and **2** were synthesized according to Scheme 1 in the text. <sup>1</sup>H NMR spectra were measured on a Bruker AV300 and a JEOL JNM-AL300 apparatus. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer and a Bruker Daltonics autoflex III.

## 2. Preparation of ionic monomers and gels

### Synthesis of compound 2

A mixture of tri-(*n*-hexyl)amine (5.40 g, 20.0 mmol) and 4-(chloromethyl)styrene (9.16 g, 60.0 mmol) and DMF (40 ml) was stirred at 60 °C for 48 h under Ar atmosphere. The solvent was removed by a rotary evaporator, and the viscous liquid was purified by reprecipitation into excess amount of hexane to yield **2** as a white powder ( 7.6 g, 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS standard, r.t.)  $\delta$  = 0.89(t, *J*=6.3 Hz, 9H NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.28(m, 18H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.77(m, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.32(m, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.99(s, 2H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHCH<sub>2</sub>), 5.35(d, *J*=10.8, 1H, alkene*H*), 5.82(d, *J*=17.7, 1H, alkene*H*), 6.71(dd, *J*=10.8, 1H, alkene*H*) 7.49(d, *J*=8.1, 2H, Ph*H*) 7.52(d, *J*=7.8, 2H, Ph*H*). MS (MALDI-TOF):*m/z* calcd for C<sub>27</sub>H<sub>48</sub>N<sup>+</sup> : 386.68; found: 386.67

### Synthesis of Compound 1

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (10.6 g, 12.0 mmol) and **2** (5.07 g, 12.0 mmol) was dissolved in methanol (20 mL). Water was added dropwise to the stirring solution, and white solid gradually precipitated. The resulting mixture was stirred for more 3 hours. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO<sub>2</sub>, dichloromethane) to yield **1** as a white solid. (12.1 g, 80%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS standard, r.t.)  $\delta$  = 0.88(t, *J*=6.9 Hz, 9H NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.32(m, 18H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.72(m, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.96(m, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.16(s, 2H, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHCH<sub>2</sub>), 5.43(d, *J*=10.8, 1H, alkene*H*), 5.85(d, *J*=17.7, 1H, alkene*H*), 6.70(dd, *J*=10.8, 1H, alkene*H*), 7.18(d, *J*=8.1, 2H, Ph*H*), 7.52(m, 6H, Ph*H*), 7.69(s, 8H, Ph*H*). MS (MALDI-TOF): calcd for C<sub>27</sub>H<sub>48</sub>N<sup>+</sup> : 386.68; found: 386.67, C<sub>32</sub>H<sub>12</sub>BF<sub>4</sub><sup>-</sup> 863.21; found 862.53.; elemental analysis : calcd(%) for C<sub>59</sub>H<sub>60</sub>BF<sub>24</sub>N: C 56.70, H 4.84, N 1.12; found: C 56.75, H 4.84, N 1.19

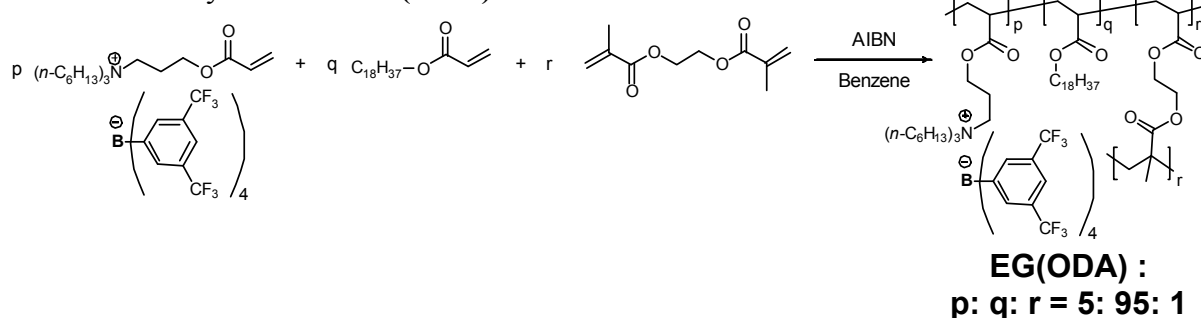
## Preparation of Gels

Gelation conditions are summarized in Table S1. A typical protocol is as follows; 187 mg (0.15 mmol) of **1**, 505 mg (4.85 mmol) of styrene, 6.50 mg (0.05 mmol) of divinylbenzene (DVB), and 8.21 mg (0.05 mmol) of AIBN were placed in a glass tube and dissolved in THF 500  $\mu$ l. 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 = 3:97:1. 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(PS)** and **NG(PS)**.

entry	<b>1</b> (mol/L)	Styrene (mol/L)	DVB (mol/L)	AIBN (mol/L)
<b>EG(PS)</b>	0.30	9.70	0.10	0.10
<b>NG(PS)</b>	0	10.0	0.10	0.10

### Scheme S1. Synthesis of **EG(ODA)**



### 3. Measurement of Swelling Degrees

A sliced gel was placed in the following typical organic solvents with various polarities; toluene (dielectric constant  $\epsilon = 2.4$ ), chloroform ( $\epsilon = 4.8$ ), ethyl acetate ( $\epsilon = 6.0$ ), tetrahydrofuran (THF) ( $\epsilon = 7.6$ ), 2-octanol ( $\epsilon = 8.2$ ), dichloromethane ( $\epsilon = 8.9$ ), 1,2-dichloroethane ( $\epsilon = 10.4$ ), 2-octanone ( $\epsilon = 10.4$ ), 1-butanol ( $\epsilon = 17.5$ ), acetone ( $\epsilon = 20.6$ ), ethanol ( $\epsilon = 24.6$ ), methanol ( $\epsilon = 33.0$ ), *N,N*-dimethylformamide (DMF) ( $\epsilon = 37.0$ ), and dimethylsulfoxide (DMSO) ( $\epsilon = 47.0$ ). After immersion for 2 days, we measured the swelling degrees ( $Q$ ) of the gels defined as the following equation;  $Q = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}$  (wt / wt) where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  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. The swelling degrees of **EG(PS)** and **NG(PS)** in various organic solvents are shown in Table 1.

#### Reference

- 1 D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 3810.