

Strategy for preparation of hybrid polymer hydrogels using silica nanoparticles as multifunctional crosslinking points

Makoto Takafuji, Shin-ya Yamada and Hirotaka Ihara*

ESI-1: Typical preparation procedure of *pSi-VPx*

Copolymerization of *N*-vinylpyrrolidone (**VP**) and 3-methacryloxypropyltrimethoxysilane (**Si**) was initiated by 2,2-azobis(isobutyronitrile) (AIBN) as a radical initiator in ethanol solution. Typical polymerization condition is as follows: 5.56 g (50 mmol) of VP, 0.117 g (0.5 mmol) of Si and 17 mg (0.3 wt% of monomer) of AIBN were dissolved in 30 mL ethanol. The solution was heated to 60 °C and mixed under nitrogen atmosphere. After 6 hours the reaction mixture was cooled to room temperature and added diethyl ether to obtain white precipitate. The precipitate was washed several times with diethyl ether and dried under vacuum. Yield: 55.6%. Preparation conditions of the polymers used in this study are listed in Table S1. The obtained polymers were characterized by ¹H NMR spectroscopy (See Fig. S1).

Table S1 Preparation conditions of *pSi-VPx*

Copolymer	VP	Si	AIBN	Ethanol	Yield
<i>pVP</i>	5.56 g (50 mmol)	-		30 mL	74.6%
<i>pSi-VP41</i>	5.56 g (50 mmol)	0.234 g (1 mmol)		30 mL	56.7%
<i>pSi-VP79</i>	5.56 g (50 mmol)	0.117 g (0.5 mmol)	17 mg (0.3 wt%)	30 mL	55.6%
<i>pSi-VP88</i>	5.56 g (50 mmol)	0.117 g (0.5 mmol)		10 mL	89.1%
<i>pSi-VP120</i>	5.56 g (50 mmol)	0.078 g (0.33 mmol)		30 mL	77.7%

ESI-2: Composition of *pSi-VPx*

The composition of *pSi-VPx* was determined by the integration ratio of Si-CH₂ (**E** in Fig. S1) of **Si** and N-CH₂ (**C** in Fig. S1) of **VP** in the ¹H-NMR spectrum which is recorded by JNM-EX400 (JEOL Co., Ltd.). Fig. S1 shows typical ¹H-NMR spectrum of *pSi-VP79*.

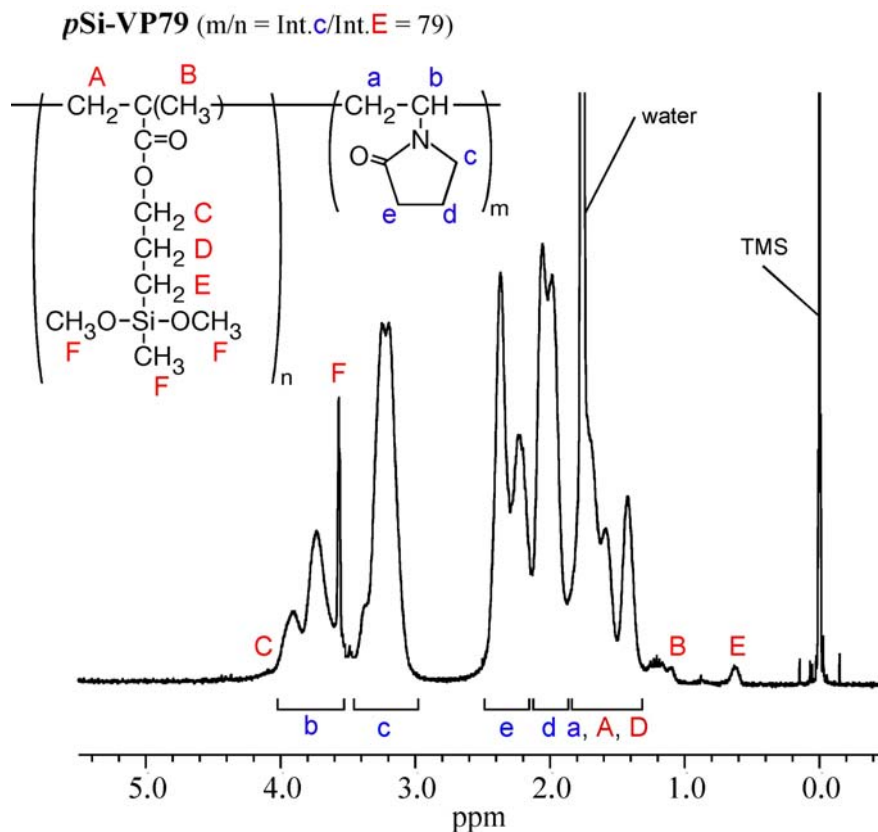


Fig. S1 ¹H NMR spectrum of *pSi-VP79*.

ESI-3: Molecular weight of *pSi-VPx* and *pSi*

The polymerization degree and polydispersity of *pSi-VPx* were determined by size exclusion chromatography (SEC). SEC system consists of a JASCO PU-2089 plus intelligent HPLC pump with a JASCO AS-2057 plus sample injector, a JASCO refractive index detector JASCO co-2065 plus and a personal computer with JASCO-ChromNAV (Ver. 1.8) software. The column temperature was maintained by using a column jacket and controlled at 30 °C. Chromatograms were recorded using TOSOH SEC column (Shodex OHpak SB-806M HQ) with HPLC grade CH₃CN and 10 mM NaCl aqueous solution mixture (10 : 90) at a flow rate 0.75 mL min⁻¹. Polyethylene oxides (TOSOH Co.) were used as a standard.

Fig. S2 shows the chromatograms of *pSi-VPx* and *pVP*, and calibration curve.

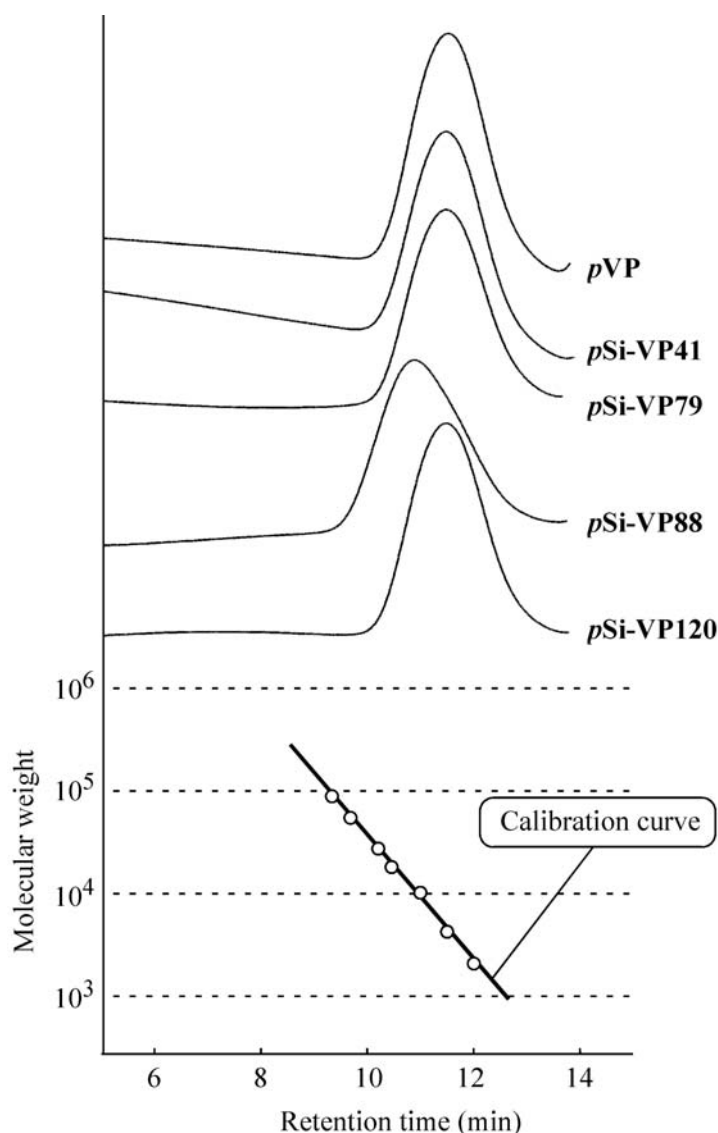


Fig. S2 SEC Chromatograms of polymers (*pSi-VPx* and *pVP*).
Column: Shodex OHpak SB-806M HQ, Mobile phase: CH₃CN/10 mM NaCl aq. (10 : 90), Flow rate: 0.75 mL min⁻¹.
Standard polyethylene oxides (TOSOH Co.): 2.1×10^4 , 4.3×10^4 , 10.1×10^4 , 1.85×10^5 , 2.72×10^5 , 5.80×10^5 and 8.95×10^5 .

ESI-4: Effect of pH on the gelation time

Table S2 Effect of pH on the gelation time of *pSi-VPx* with and without **SiNP-d**

pH	Gelation time ^a							
	5.9	7.0	7.7	8.4	9.2	9.8	10.3	11.0
<i>pSi-VP69</i> / SiNP-12.2	2 h	30 min	15 min	5 min	10 min	15 min	1 h	1 day
<i>pSi-VP69</i>	-	no gelation ^b	no gelation ^b	no gelation ^b	no gelation ^b	no gelation ^b	no gelation ^b	-

^a Gelation was tested by inversion method at 25 °C. ^b No gelation was observed within 1 week.

ESI-5: Transmission electrom microscopic images

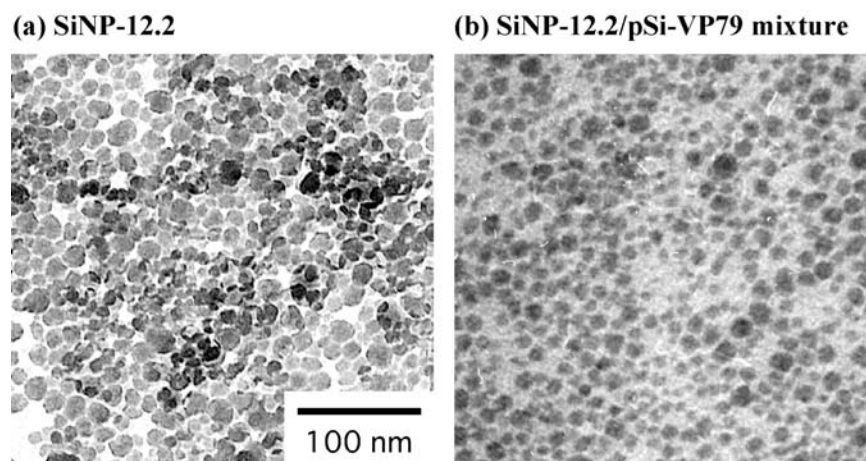


Fig. S3 TEM images of the cast film from silica nanoparticle aqueous solutions (a) without and (b) with copolymer.
[SiNP-12.2] = 15 wt%, [*pSi-VP79*] = 5 wt%,

ESI-6: Mechanical strength of the hybrid hydrogel

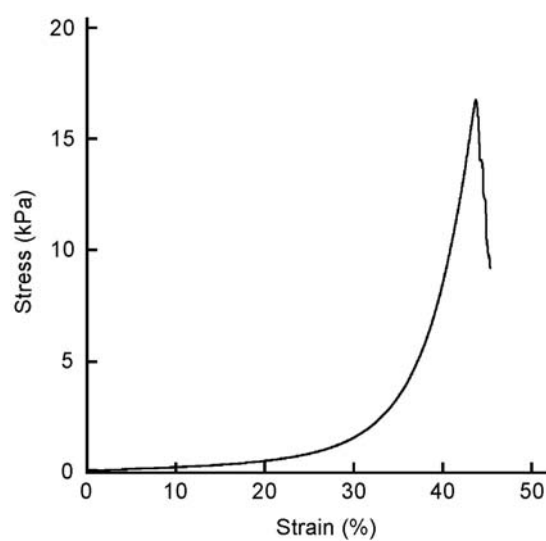


Fig. S4 Compressive strength of the hybrid hydrogels.
[SiNP-12.2] = 10 wt%, [*p*Si-VP79] = 10 wt%, Sample: 8 mm ϕ \times 8 mm.