

Electronic Supplementary Information

Water-Soluble Aromatic Polyamide for New Polymer Hydrogelator with Thixotropic Nature

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Materials and Methods

1,4-Diphenylamine (97%, Tokyo Chemical Industry Co., Ltd. (TCI)), lithium chloride (98%, TCI), *N*-methyl-2-pyrrolidone (Super Dehydrated, Wako Pure Chemical Industries, Ltd.), monosodium 2-sulfoterephthalate (98%, TCI), triphenylphosphite (97%, Sigma-Aldrich Co. LLC.) were used without further purification. All other solvents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K.).

¹H-NMR and ¹³C-NMR spectra were acquired using an AVANCE 500 (500 MHz, Bruker BioSpin K. K.) spectrometer. Elemental analysis was performed with a JM10 elemental analyzer (J-SCIENCE LAB CO., Ltd.). Size exclusion chromatography was performed using an HLC-8320 GPC EcoSEC system (Tosoh Corporation) equipped with TSK-GEL PW columns (G3000PW_{XL} and G6000PW_{XL}, column temperature: 40°C), 20 mM aqueous NaNO₃ as the eluent (0.1 ml min⁻¹) and the Shodex STANDARD P-82 series (Pullulan standard, Showa Denko K. K.) as the standards.

The gelation tests were performed using the vial inversion method in a vial with a rubber seal

(mighty vial, no. 01; Maruemu Corporation). Pale yellow solid **NaPPDT** was placed in a vial containing water to yield a specific concentration (wt%), and the vial was capped. The vial was then heated in a dry bath at 90°C until the solid **NaPPDT** was dissolved, at which point the **NaPPDT** aqueous solution was allowed to stand for 1 h at room temperature. Gelation was determined by visually observing the vial after inversion. If the mixture did not drop, the mixture was considered to have formed a gel.

The hydrogel was observed using a Leica DM2500 (Leica Microsystems) polarized optical microscope under crossed-Nicols condition.

Thixotropic behaviour was evaluated using the vial inversion method. The prepared hydrogel in the vial was shaken and mechanically collapsed using a vortex genie (Scientific Industries, Inc). The obtained sol was then allowed to set for a given time at room temperature, and the recovery of the gel state from the sol state was determined by visual observation after inversion of the vial.

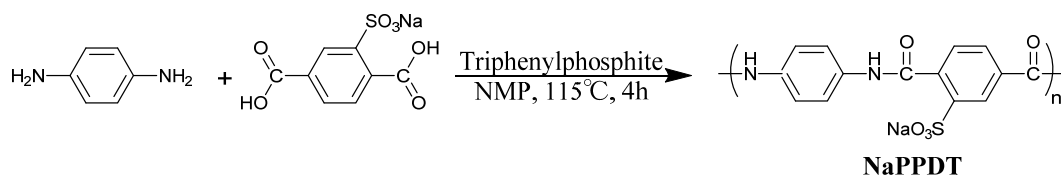
Scanning electron microscopy (SEM) images were recorded using an SU-8000 scanning electron microscope (Hitachi High-Technologies Corporation) at 1.0 kV; the SEM sample (xerogel of hydrogel) was freeze-dried and placed on a conductive tape on the SEM sample stage. Pt, as a conductive material, was used as a coating (10 nm-thick) on the sample.

Rheological measurements of the frequency sweep were performed at 25°C using an MCR-301 rheometer (Anton Paar Japan K.K.) with a parallel plate (8 mm diameter) at a gap of 0.50 mm and γ of 0.01%. Rheological measurements of the strain sweep were performed at 25°C using an MCR-301 rheometer with a parallel plate (8 mm diameter) at a gap of 0.50 mm and a constant angular frequency of 1 rad s⁻¹. For the rheological measurements, the hydrogel sample was applied onto the parallel plate and sample stage and then any overflow gel was swept away. Step-shear measurements were carried out by repeatedly applying a small strain (strain amplitude 0.01% and frequency 1 Hz) and a large strain (shear rate 3000 s⁻¹ for 0.1 s). All rheological measurements were carried out within a solvent trap made of a metal and plastic cover and the sample was surrounded by the water-wet sponge supplied by Anton Paar Japan K.K to suppress water evaporation from the sample.

Infrared spectroscopy was performed using an FT/IR-620 (JASCO Corporation) and the ATR method (ZnSe prism).

Small angle x-ray scattering (SAXS) data were recorded on a D8 Discover X-ray diffractometer (Bruker AXS K.K.) using CuK α at 26°C (the sample was placed in a 2 mm-diameter quartz glass capillary tube).

Synthesis of NaPPDT



NaPPDT was synthesised via polycondensation of phenylenediamine and sodium 2-sulfoterephthalate (instead of 2-sulfoterephthalic acid) with LiCl in *N*-methyl-2-pyrrolidone (NMP) using the phosphorylation method as reported in the literature.¹

Under an N₂ atmosphere, triphenylphosphite (10.75 g, 33.6 mmol) was added to a mixture of sodium-2-sulfoterephthalate (4.00 g, 14.3 mmol) and LiCl (12.00 g) in NMP (140 ml) at 40°C, and then the mixture was stirred for 15 min. To this solution was added 1,4-phenylenediamine (1.63 g, 14.3 mmol), and the resultant mixture was stirred at 115°C for 4 h.

Once the reaction was complete, the mixture was poured into methanol (1500 ml) to cause precipitation of the product, which was then vacuum dried. The dried **NaPPDT** was then dissolved in NMP (400 ml) and precipitated a second time by pouring this solution into acetone (6 L). This precipitate was also vacuum dried. The dried **NaPPDT** was subsequently dissolved in deionised water and dialysed using FisherbrandTM regenerated cellulose dialysis tubing (molecular weight cut off: 3500 Da, Fisher Scientific) for one week. The water was then removed from the solution *in vacuo*, and **NaPPDT** (4.76 g, yield 93.9%) was obtained as a pale yellow solid after vacuum drying.

NaPPDT: ¹H-NMR (500 MHz, DMSO-*d*₆, TMS, δ, ppm): 11.34 (s (br), 1H), 10.55 (s (br), 1H), 8.50 (s (br), 1H), 8.17–7.69 (m, 6H). ¹³C-NMR (125 MHz, DMSO-*d*₆, TMS, δ, ppm): 193.81, 193.22, 145.28, 131.55, 130.31, 129.22, 127.36, 121.83, 121.69, 121.27, 121.00, 120.89. Elemental anal. calcd for C₁₄H₉N₂O₅SNa (monomer unit): C, 49.41; H, 2.67; N, 8.23. Found: C, 49.30; H, 3.18; N, 8.24.

Figs S1 and S2

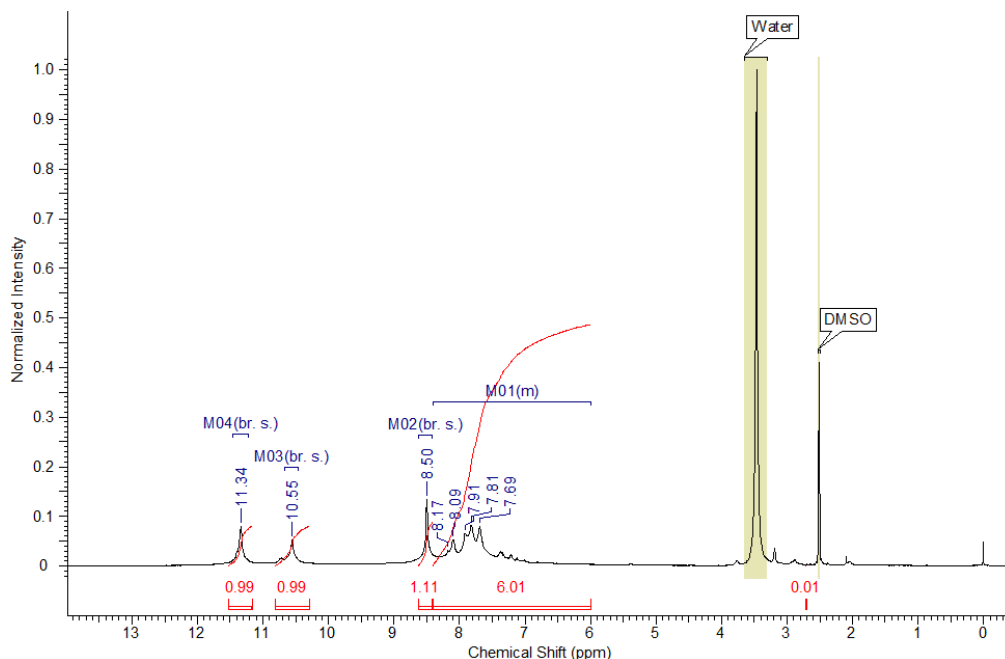


Fig. S1 ^1H -NMR spectrum of NaPPDT in D_2O (created using the ACD/NMR Processor Academic Edition). The peak at 2.70 ppm is due to the methyl proton of NMP. On the basis of these results, the residual NMP content in the NaPPDT ($-\text{CH}_3$: 2.70 ppm) was calculated to be $<1.0\%$.

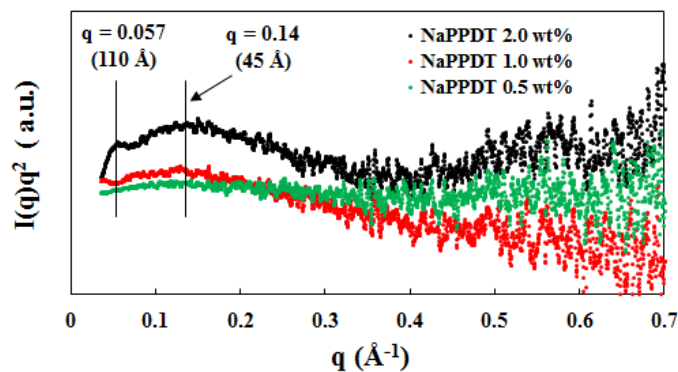


Fig. S2 Kratky-type plots of the small-angle X-ray scattering (SAXS) data for the NaPPDT hydrogels. To obtain structural information for the hydrogels, SAXS analyses were performed. Peaks associated with the long-range structure of the hydrogels were observed that may be related to their anisotropic structure (see Figs 1 and 2).

Figs S3 and S4

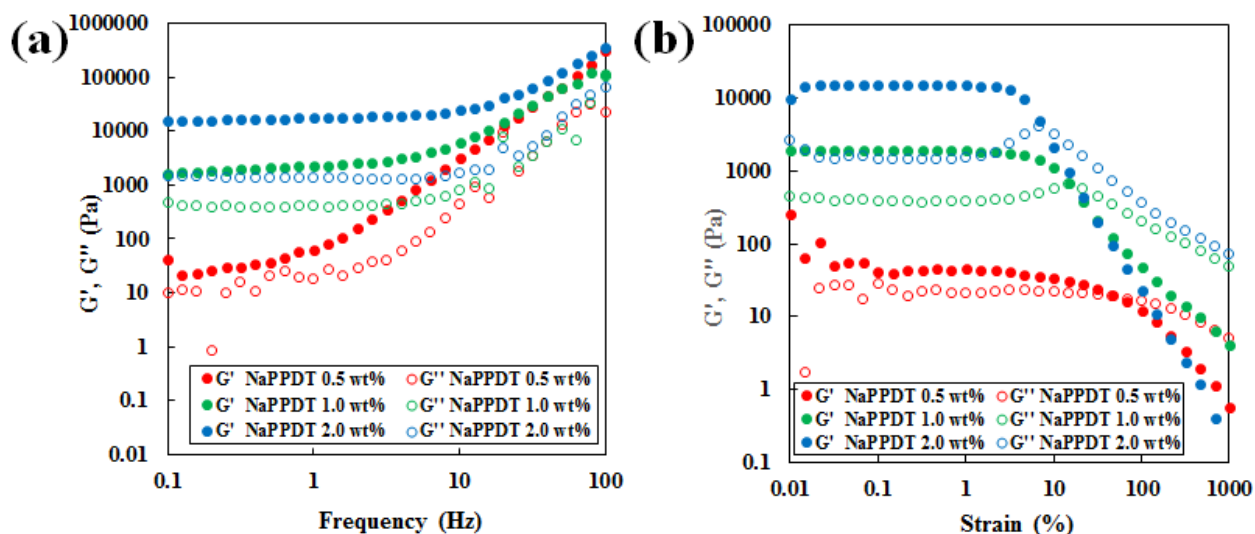


Fig. S3 Dynamic rheological properties of the NaPPDT hydrogels: (a) Frequency sweep and (b) strain sweep. These results confirmed the existence of a stable gel state ($G' > G''$) in the hydrogels with >1.0 wt% NaPPDT and also indicated that the NaPPDT 2.0 wt% hydrogel possessed a higher G value (stiffer material) than that of the NaPPDT 1.0 wt% hydrogel.

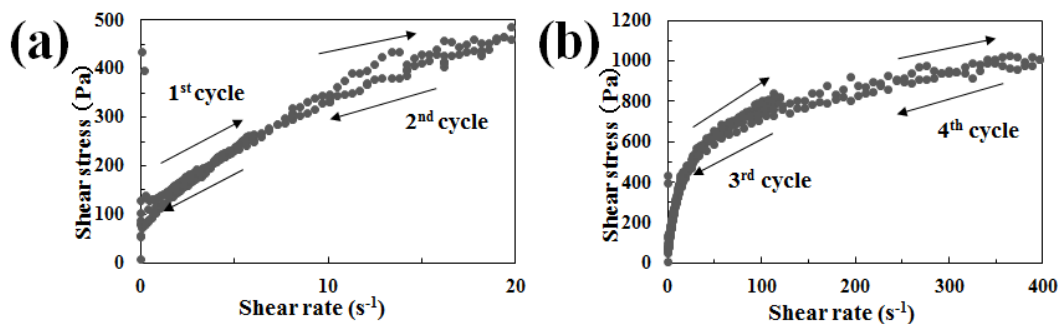


Fig. S4 Thixotropic hysteresis loop of NaPPDT hydrogel. The test was conducted with 1st cycle: $0.001 s^{-1} \sim 5.0 s^{-1} \sim 0.001 s^{-1}$ (120 s), 2nd cycle: $0.001 s^{-1} \sim 20 s^{-1} \sim 0.001 s^{-1}$ (120 s), 3rd cycle: $0.001 s^{-1} \sim 100 s^{-1} \sim 0.001 s^{-1}$ (120 s), 4th cycle: $0.001 s^{-1} \sim 400 s^{-1} \sim 0.001 s^{-1}$ (120 s), with 1 min intervals between cycles.

Fig. S5

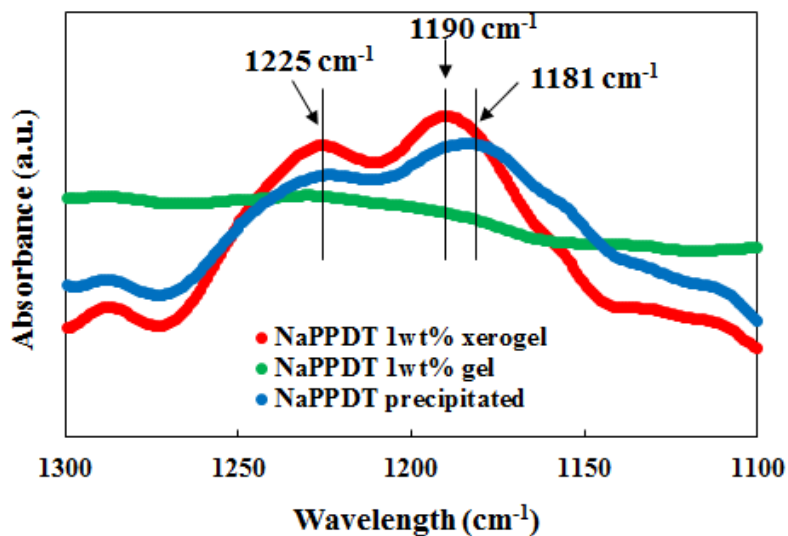


Fig. S5 IR spectra of the NaPPDT aqueous solution in the region of sulfonyl stretching.

Acknowledgements

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