Supporting Information for

Dehumidification at high temperature and high humidity by low-temperature regenerative polymers

Hidenobu Wakita [*a], Yasuaki Okumura [a]

[a] *Technology Division, Panasonic Corporation, Seika-cho, Soraku-gun, Kyoto 619-0237, Japan*

[*] Corresponding author. E-mail address: hwakita@mtj.biglobe.ne.jp (H. Wakita)

Synthesis procedure

N-acryloylglycinamid (NAGA): N-acryloylglycinamide was prepared according to literatures. [1-3] In a 1 L three-necked round-bottom flask equipped with a magnetic stirrer and placed in an ice bath, glycinamide hydrochloride (67.9 g, 0.615 mol) and 65 mL of cool distilled water were introduced, and the mixture was stirred with flowing N_2 to the flask. Then, 194 mL of cool diethyl ether and 360 mL of cool 2 M potassium carbonate solution were introduced prior to dropwise addition of a solution of freshly distilled acryloyl chloride (61.5 g, 0.679 mol) in 258 mL of diethyl ether. The mixture was kept at 5°C for 30 min with being stirred during the addition of acryloyl chloride, and stirred for 2 h at room temperature. Then, the pH of the medium was set at 2 by the addition of 6 N HCl, and the ether layer was removed. The aqueous medium was washed three times with 190 mL of diethyl ether. The remaining traces of diethyl ether was removed under slight dynamic vacuum at room temperature, and the pH was increased to neutral with 2 N NaOH. Then, the mixture was freeze-dried to yield 196 g of a mixture of NAGA and potassium chloride, which was washed three times with 1.6 L of 4/1 V/V ethanol/methanol mixture to remove the organic salt. The solution was

evaporated, and the crude product was dissolved in 1 L of 1/4 V/V methanol/dichloromethane mixture by heating it to reflux it. The solution was filtered to remove polymeric impurities and purified by column chromatography (d = 3.3 cm, 343 mL silica, porosity 60Å, 0.06 - 0.2 mm mesh size, TLC: Rf(NAGA) = 0.47) to obtain 11.7 g (yield 15 %) of the product, which was recrystallized from 184 mL of 1/2 V/V methanol/acetone mixture.

Poly(N-acryloylglycinamide-co-acrylonitrile) (PNAGAAN): Poly(N-acryloylglycinamide-co-acrylonitrile) was prepared according to a literature.[4] Polymerization was carried out under Ar. NAGA, freshly-distilled acrylonitrile (AN) (in total 26 mmol) and *S*-cyanomethyl-*S*-dodecyltrithiocarbonate (CMDT) (0.13 mmol) were dissolved in 41.5 mL of DMSO (feed ratio NAGA/AN = 69/31 ~ 65/35) in a Schlenk flask followed by three freeze-pump-thaw cycles. Then, an AIBN/DMSO (0.04 mmol of AIBN) was added and the polymerization was carried out in an oil bath at 70°C. The polymer was precipitated from tenfold volume methanol and was centrifuged (10000 rpm, 10 min). Next, it was washed three times with methanol, dried in a vacuum oven at 70°C for 24 h, and crushed by a motor and pestle. Fig. S1 shows a photograph of the powder before the water adsorption, and it changed to hydrogel after the first water adsorption.
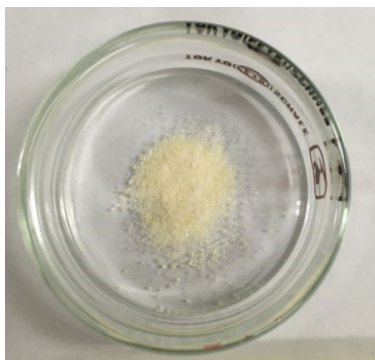

Fig. S1. Photograph of PNAGAAN-33 before the water adsorption test.

Poly(N-acryloylglycinamide) (PNAGA): Poly(N-acryloylglycinamide) was prepared according to a literature.[5] In a glass test tube, NAGA (0.5 g, 3.9 mmol) and N,N'-methylene bis(acrylamide) (6 mg, 0.039 mmol) were dissolved in 1.9 mL of DMSO and purged with N_2 for 30 min. A DMSO solution (100 µL) containing 3.5 mg AIBN was added and the tube was quickly heated to 70°C. After 2 h, the tube was quickly cooled to room temperature and broken to retrieve the polymer gel. The gel was purified by dialysis against deionized water (2 L water, three times exchanged, for 4 days), and dried in a vacuum oven at 65°C for 24 h and crushed by a motor and pestle.

Infrared spectroscopy (IR)

The Spectrum was recorded by a FTIR spectrometer (Thermo Fisher Scientific, Nicolet 6700) with an attenuated total reflectance (ATR) unit. The spectrum of PNAGAAN-33 is shown in Fig. S2.
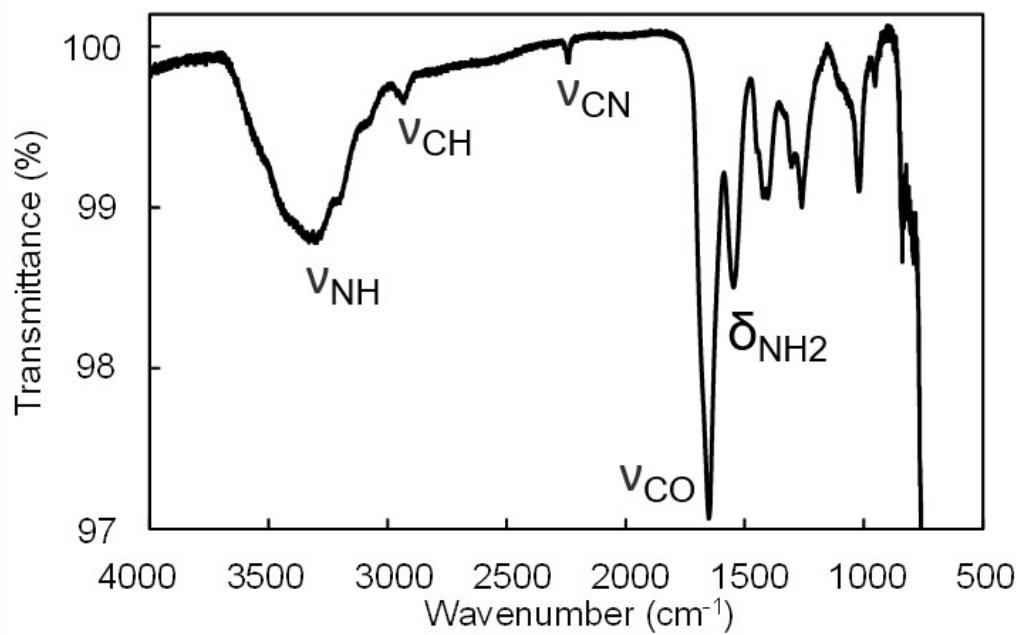
Fig. S2. IR spectrum of PNAAAN-33.

Nuclear magnetic resonance spectroscopy (NMR)

A Jeol ECZ600R (600 MHz) was used for the measurement of ^{1}H NMR spectrum. The spectrum of PNAGAAN-33 is shown in Fig. S3.
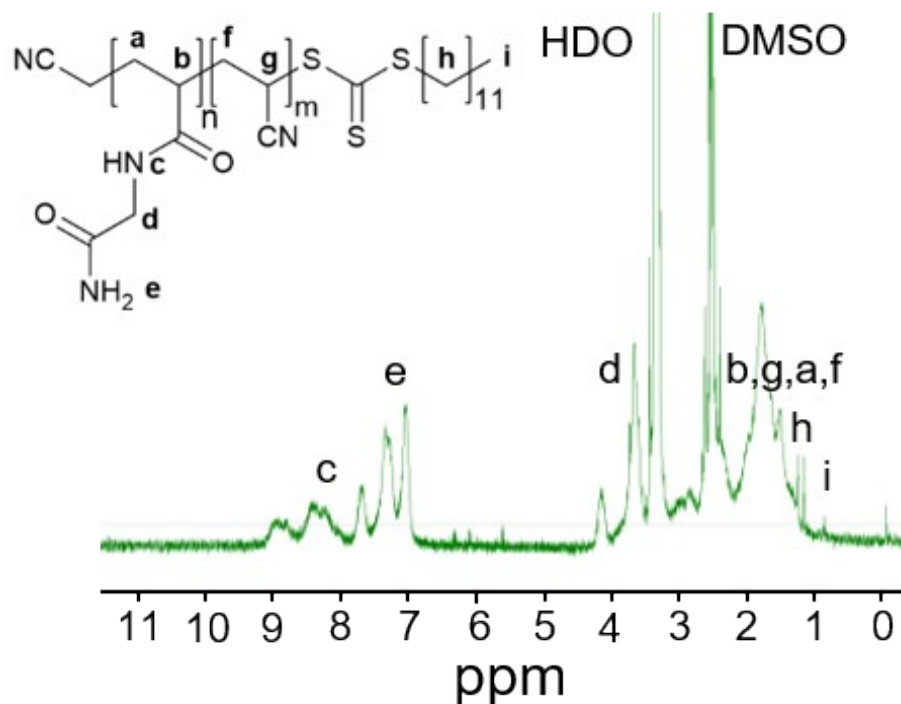
Fig. S3. ^{1}H NMR spectrum of PNAGAAN-33 in DMSO-d_6.

Gel permeation chromatography (GPC)

The GPC measurement with DMSO containing 10 mM LiCl as effluent was carried out to determine the molar weight and the molar weight distribution of PNAGAAN-33 by using a Tosoh KLC-8320GPC with a differential refractive index detector. A precolumn (TSKgel guardcolumn α, dimension 6 mm x 40 mm) and two TSKgel α-M (dimension 7.8 mm x 300 mm) columns were used. The flow rate was 0.8 mL/min at 60°C. Pullulans of different molar masses with narrow dispersities were used as standards. The GPC of PNAGAAN-33 showed molar mass of 8400 g/mol and mass dispersity of 1.5 as shown in Fig. S4.
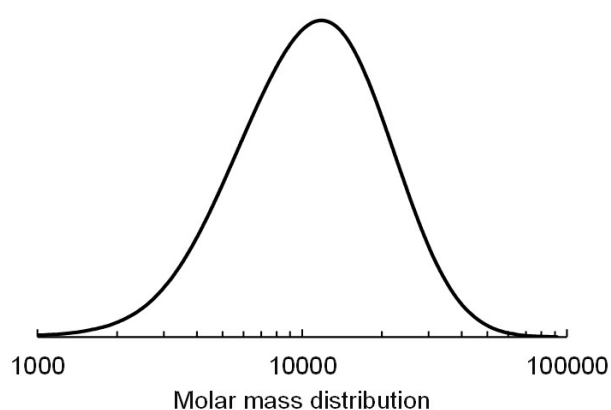
Fig. S4. GPC curve of PNAGAAN-33 in DMSO with 10 mM LiCl.

Differential scanning calorimetry (DSC)

A Hitachi DSC7020 system was used for DSC measurement under N_2 flow with a heating and cooling rate of 10 and 20°C/min, respectively. For the measurement, 2.3 mg of PNAGANAAN-33 was used, and the second heating cycle was analyzed (Fig. S5).
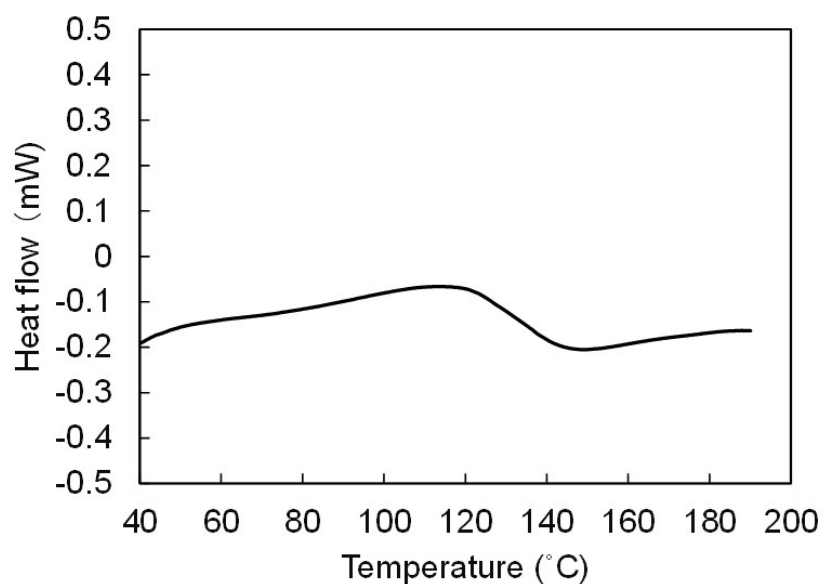

Fig. S5. DSC result of PNAGAAN-33. Heating rate is 10˚C/min. The Tg was determined from the second heating curve.

Scanning electron microscopy (SEM) images

The SEM images of PNAGAAN-33 was obtained by a high resolution field emission scanning electron microscope (Hitachi, SU8220) without any coating. Fig. S6 shows a representative SEM image.
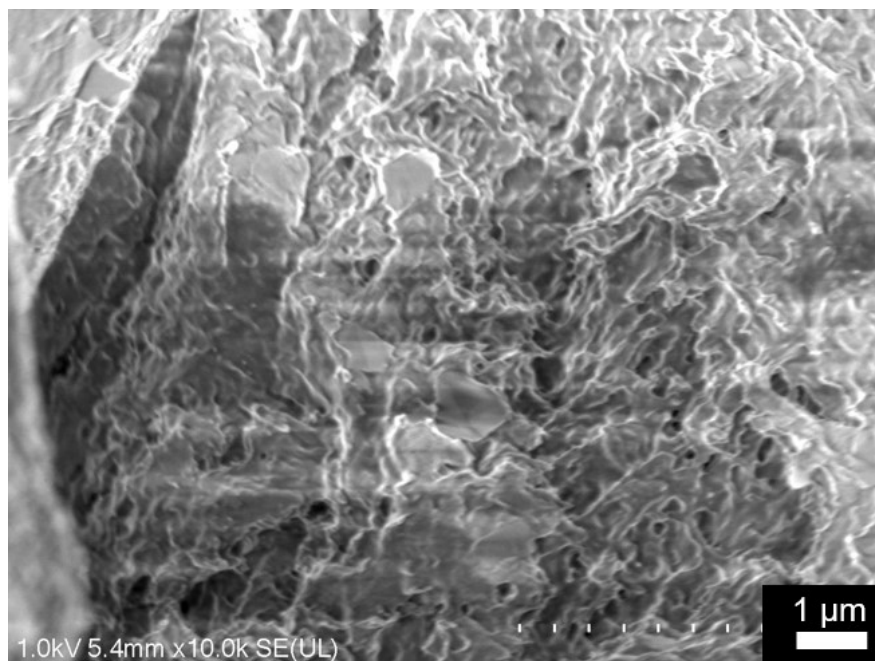

Fig. S6. SEM image of PNAGAAN-33.

Turbidity measurement

To determine the UCST of PNAGAAN, changes in percent transmittance at 660 nm were measured as a function of temperature for aqueous solution. An Ophir NOVAII was used as the detector. The cell path length was 10 mm, and the solution was stirred at a heating/cooling rate of 1°C/min. The cloud points were determined from the temperature at the transmittance of 50%. Fig. S7 shows the results of PNAGAAN-35 and PNAGAAN-31. For the first heating of both samples, high transmittance was observed even at low temperature, and then the relatively stable transmittance curves were repeated.
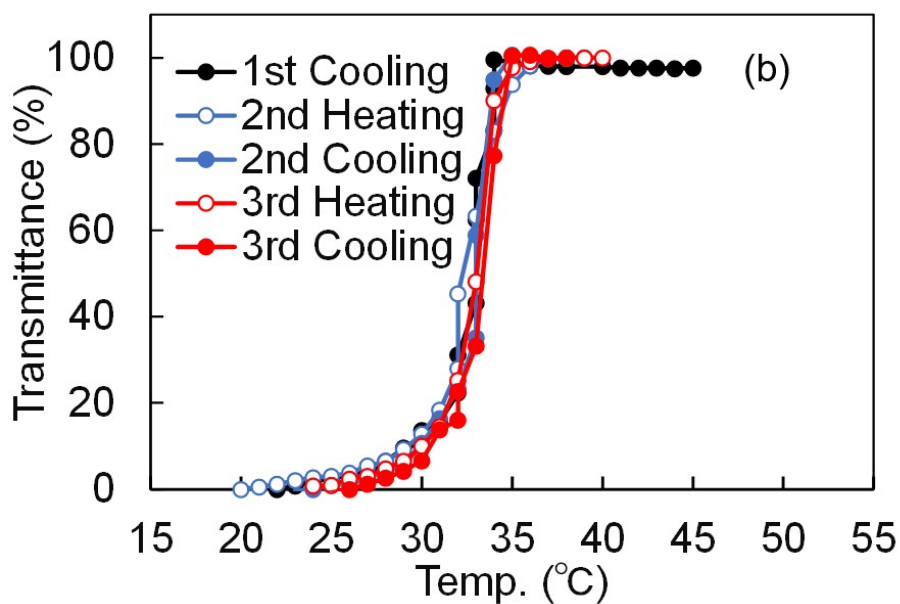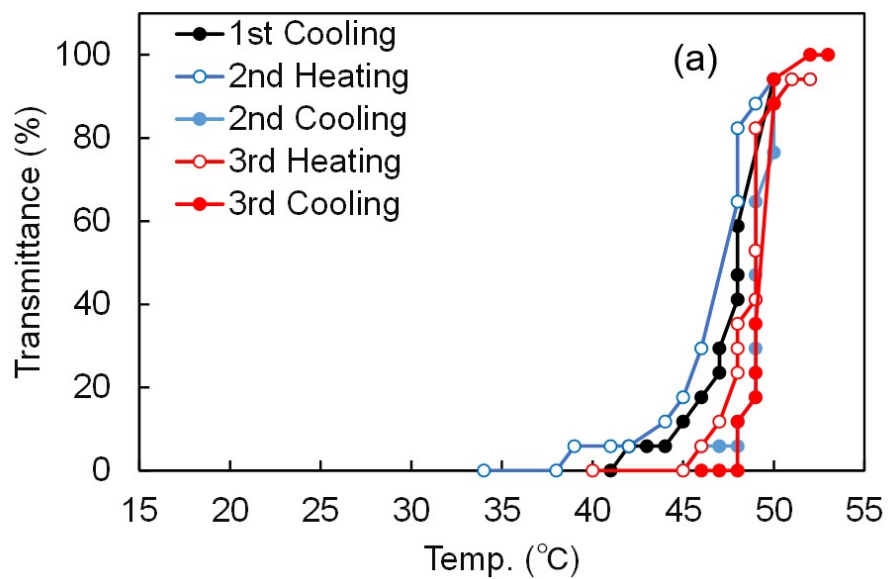
Fig. S7. Transmittance curves of 1 wt% aqueous solution of PNAGAAN-35 (a) and PNAGAAN-31 (b).

Water adsorption measurement

The water adsorption isotherms were measured by means of a volumetric method using a MicrotracBEL Belsorp-Max II. Prior to each measurement, the polymer specimen was dried *in vacuo* at 70°C for 6 h. For the B-type silica gel (Fuji Sylisia,

Sylisia 350), it was pretreated at 150°C. In this study, the same specimen was used for all isotherms at different temperatures, and was pretreated before each isotherm was taken. We confirmed that the isotherms were reproducible by measuring the isotherms at 40 and 5°C repeatedly. The adsorption temperature was corrected by the measurement of the saturated water vapor pressure using a vacant sample tube before each test. Figs. S7 and S8 show the isotherms of PNAGAAN-35 and PNAGAAN-31, and those of PNAGA, respectively. Fig. S9 shows the isotherms including that at 20°C of PNAGAAN-33.
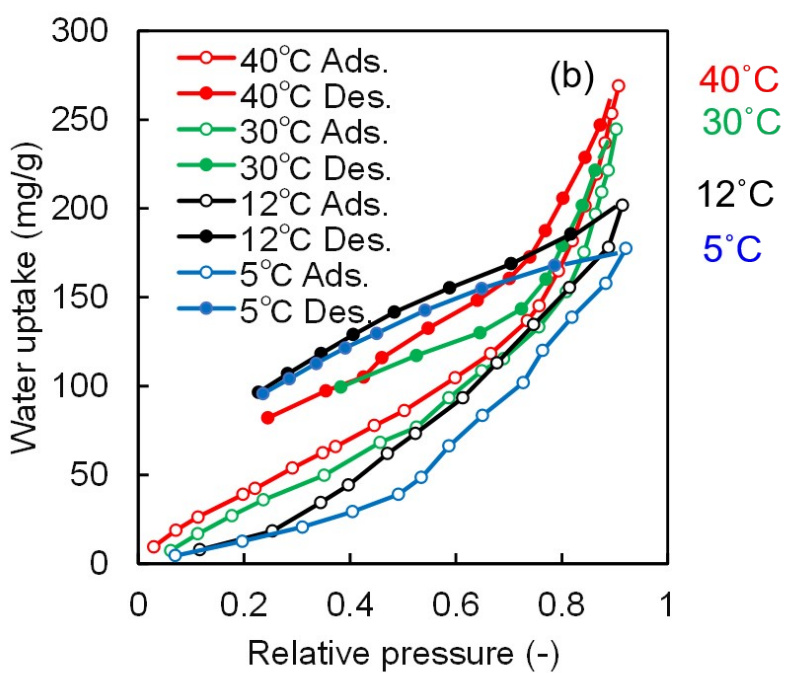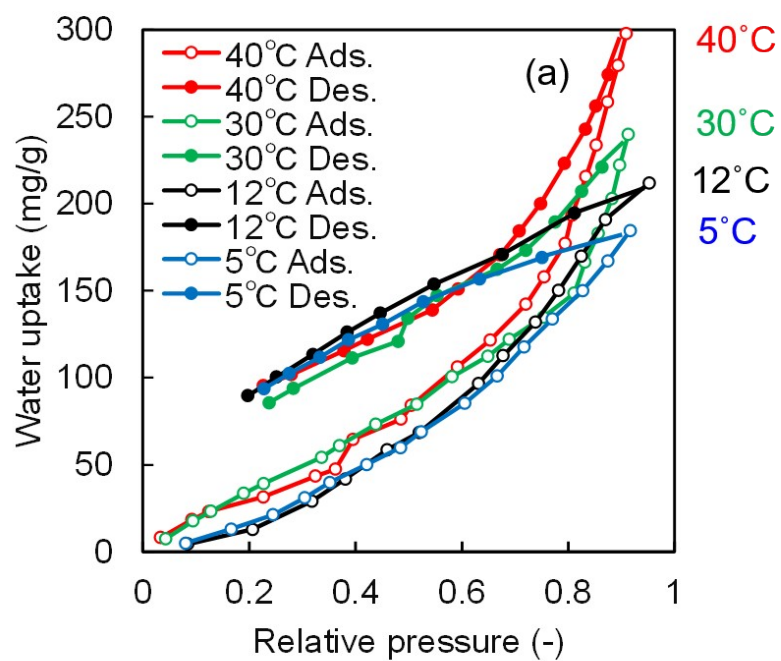
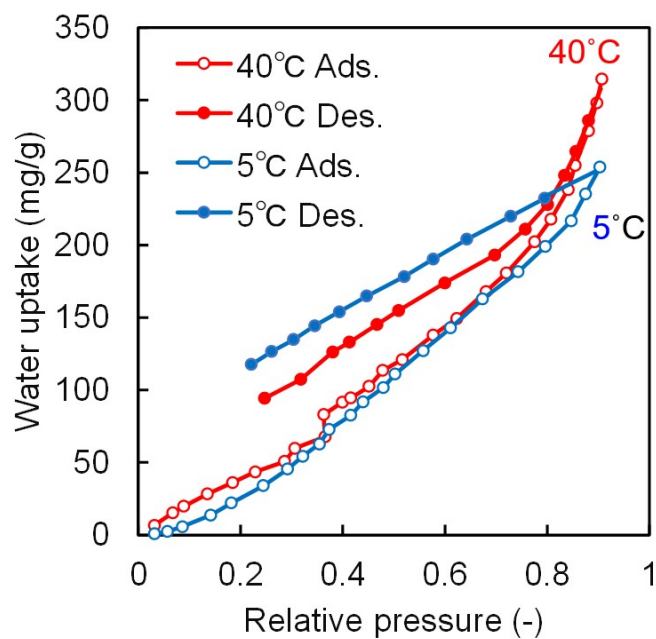Fig. S8. Water adsorption isotherms at various temperatures of PNAGAAN-35 (a) and PNAGAAN-31 (b).

Fig.S9. Water adsorption isotherms of PNAGA at 5 and 40˚C. The same sample was used for all experiments, and was pretreated before each measurement at 70˚C *in vacuo* for 6 h.
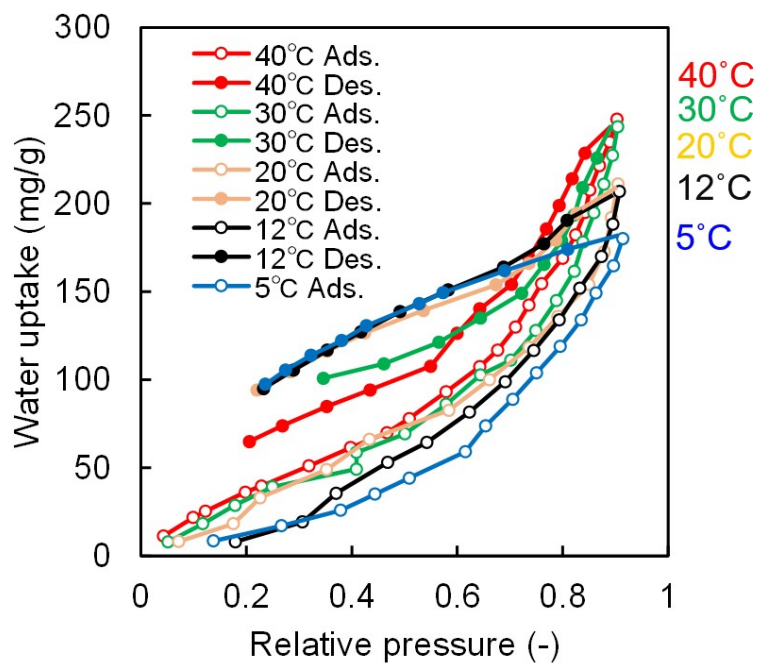

Fig. S10. Water adsorption isotherms at various temperatures of PNAGAAN-33.

Table S1. Saturated salts and their humidity for the measurements of water uptake at 5, 25 and 50°C.

Salt	Temperature		
	5°C	25°C	50°C
	Humidity (decimal)		
K_2SO_4			0.958
KNO_3	0.963	0.936	0.848
KCl	0.877		
NaCl	0.757		0.751
NaBr			0.509
K_2CO_3	0.431	0.432	

To study the regeneration at low temperature, amounts of adsorbed water on PNAGAAN-33 were evaluated at various conditions without any heat treatment. A small amount of PNAGAAN-33 put on a petri dish was placed in a desiccator with a saturated salt aqueous solution at a constant temperature to keep the humidity for a day, and then was weighed. The specimen was immediately moved to another desiccator with another saturated salt aqueous solution at a different temperature without any heat treatment, and was weighed. The desiccators for the tests were changed one after another. The humidity was controlled by various saturated salts as shown in Table S1. The degree of adsorption was evaluated by the weight ratio between adsorbed water and the weight before the first test. For the adsorption at 5°C, dry N_2 was introduced to the desiccator before closing the lid of desiccator to prevent from the water condensation of the ambient air. After an additional day, it was immediately weighed in a glovebox.

Table S2. Storage modulus and loss modulus of PNAGAAN-33 after water adsorption at 5 or 50°C and $p/p_0 = 0.96$ for one night.

Adsorption condition	E' (MPa)	E" (MPa)	tan δ
5°C, p/p_0=0.96	29*	3.3	0.12
50°C, p/p_0=0.96	0.23	0.10	0.44

The dynamic mechanical analyses were carried out at 1 Hz and at 16°C in dry air flow just after the adsorption at p/p_0=0.96 at 5 or 50°C for one nihght.

* When the maximum force was applied, the amplitude of 5 μm could not be achieved. Therefore, it equaled Young's modulus.

Dynamic mechanical analysis (DMA)

The DMA measurements were conducted for samples (thickness: ~ 1mm), which had been put on an indenter (diameter: 10mm) and kept at the humidity of $p/p_0 = 0.96$ at 5 or 50°C for one night. Then, the sample was sandwiched between a parallel plate compression clamp and an oscillatory compression with an amplitude of 5 μm and a frequency of 1 Hz up to a ceiling of a static force of 3.4 N was applied at 16°C in dry air flow using a SII DMA6000. The results were shown in Table S2. For the specimen which had been kept at 5°C and at $p/p_0 = 0.96$, the amplitude of 5 μm could not be achieved, when the maximum force was applied. Therefore, the storage elastic modulus equaled the Young's modulus.

Differential scanning calorimetry (DSC) for water adsorption

The heat of adsorption and desorption by alternate changes of N_2 flow of the humidity of $p/p_0 = 0.76$ (50 mL/min) and dry N_2 was measured using a Setram Instrumentation calvet type calorimeter C-80 equipped with a Micro Equipment moisture generator me-40DP-H90. The specimen (50 mg) was used without any heat treatment and the gas was switched after 4 h.

Adsorption rate analysis

The mass transfer coefficients through the micropores ($k_s a_p$, a_p: external surface area of particles) were estimated by linear driving force approximation,[6] in which water adsorption rate (dq/dt) is proportional to the difference between the equilibrium water adsorption amount (q^*) and the water adsorption amount (q) as the following equation.

$$dq/dt = k_s a_p (q^*-q) \quad \text{------------------------------------①}$$

The changes in the pressure during the measurement of the water adsorption isotherms by means of a volumetric method using a MicrotracBEL Belsorp-Max II were recorded and the mass transfer coefficients were fitted by a software MicrotracBEL Belmaster.

References

1.   H. C. Haas and N. W. Schuler, *J. Polym. Sci., Part C: Polym. Lett*, 1964, **2**, 1095.

2.   J. Seuring, F. M. Bayer, K. Huber and S. Agarwal, *Macromolecules*, 2012, **45**, 374.

3.   M. Boustta, P-E. Colombo, S. Lenglet, S. Poujol and M. Vert, *J. Controlled Release*, 2014, **174**, 1.

4.   F. Käffer, A. Lerch and S. Agarwal, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 274.

5.   F. Liu, J. Seuring and S. Agarwal, *Macromol. Chem. Phys.*, 2014, **215**, 1466.

6.   E. Glueckauf, *Trans. Faraday Soc.*, 1995, **51**, 1540.