Supplementary Information for

Simple preparation of supramolecular polymer gels via hydrogen bonding by blending two liquid polymers

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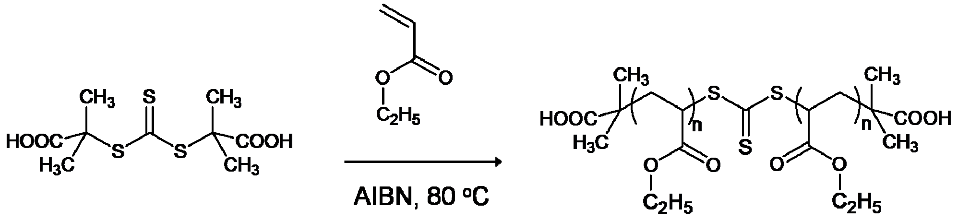
Materials.

A poly(ethyleneimine) (**PEI**, M_n ~ 1200, M_w ~ 1300, Fig. 1b) solution in water and ethyl acrylate were purchased from Aldrich and TCI, respectively. The other chemicals were purchased from Kishida Regents Chemicals, Japan. Neat poly(ethyleneimine) for blend experiments was prepared by drying the solution *in vacuo*. Ethyl acrylate was purified by passing through an aluminum oxide column before polymerization. The others were used as received.

Synthesis of Carboxyl-Terminated Telechelic Poly(ethyl acrylate) (PEA-(COOH)$_2$).

Carboxyl-terminated telechelic poly(ethyl acrylate) (**PEA-(COOH)$_2$**) was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization by using the difunctional chain transfer agent with two carboxylic acids, S,S'-bis(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (Scheme S1). Ethyl acrylate (12g, 0.12 mol) was polymerized with a difunctional RAFT agent (0.34 g, 1.19 mmol) in bulk at 80 ºC for 20 min. After deactivation of the polymer with liquid nitrogen, the polymer was purified by a reprecipitation procedure with hexane as a non-solvent and dried *in vacuo*.

Scheme S1 Synthesis of PEA-$(COOH)_2$.



Size Exclusion Chromatography (SEC).

SEC was performed to measure polydispersity of PEA-$(COOH)_2$ by using two G3000H_{HR} and one G4000H_{HR} columns (Tosoh Corp.) combined with an HPLC pump and a refractive index detector (Tosoh Corp.). Tetrahydrofuran (THF) was used as the eluent, and a flow rate was 1 ml/min. Calibration was done with polystyrene standards.

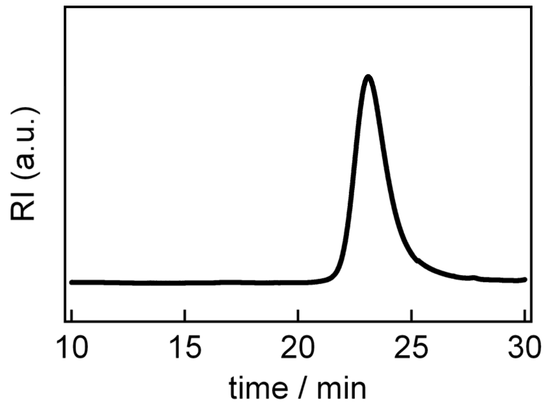


Fig. S1 SEC chromatogram of PEA-$(COOH)_2$.

^{1}H NMR.

The number-average molecular weight of PEA-$(COOH)_2$ was determined with ^{1}H NMR spectroscopy (Varian, INOVA), by end-group analysis. The molecular weight was determined by comparing the integral of peaks at 4.7 ppm from two protons at the end of the polymer adjacent to the CTA residue (S-C(=S)-S) with the integral of the peaks for the backbone methylene (2H × n) around 4.0 ppm (Fig. S2). The solvent used for the experiment was DMSO-*d6*.

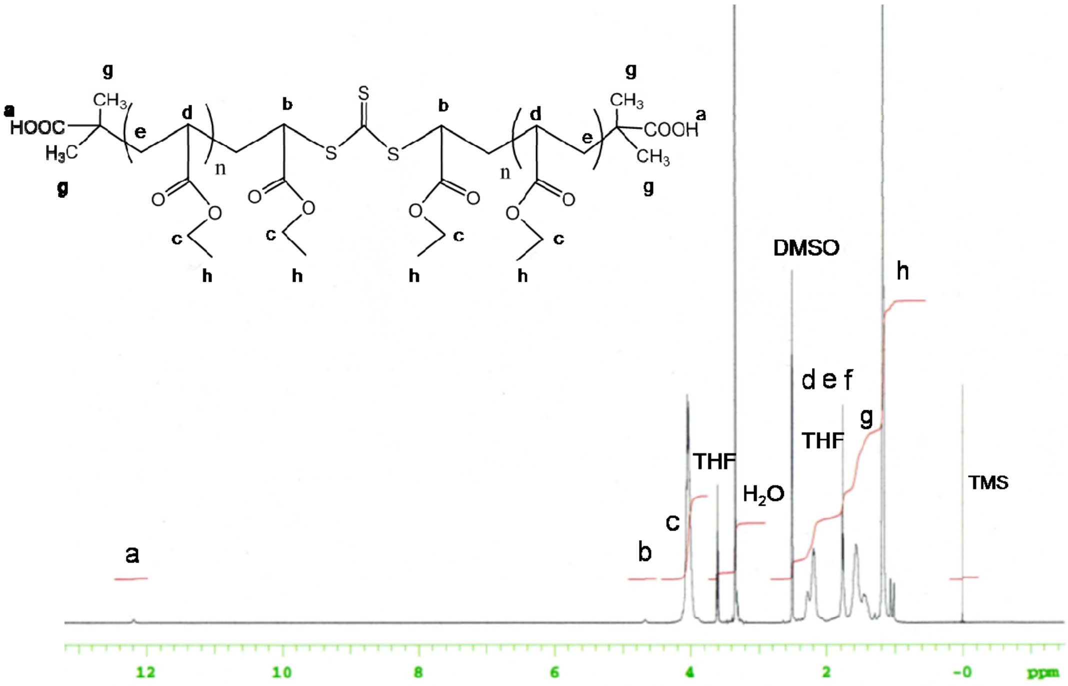


Fig. S2 ^{1}H NMR spectrum of PEA-$(COOH)_2$.

FT-IR spectroscopy.

FT-IR spectroscopy of AI-10:1 was measured at room temperature under the reduced pressure. The measurement of PEA-$(COOH)_2$ was also done as a control experiment. The instrument used for measurements was FT-IR 6100 (Jasco, Japan). Although the absorption of the carbonyl stretching of COOH in the 1700 cm^{-1} region could be an indicator of hydrogen bonding between -COOH and –NH-, the absorption of the carbonyl stretching of COOH at the both ends is much smaller than that of carbonyl stretching originated from many ester groups in PEA-$(COOH)_2$ and it can not be an precise indicator of the hydrogen bonding in this case. Therefore, we paid attention to the 3500 cm^{-1} region of the stretching vibration of hydroxyl groups. Fig. S3 shows the spectra of samples in the range of 3100 to 3600 cm^{-1} : the top for AI-10:1; the bottom for PEA-$(COOH)_2$. A sharp peak at 3441 cm^{-1} could be attributed to the absorption of the stretching vibration of free O-H on the ends of PEA-$(COOH)_2$, which was seen for both spectra of AI-10:1 and PEA-$(COOH)_2$. On the other hand, the broad peak at 3280 cm^{-1} on the spectrum of PEA-$(COOH)_2$ at the bottom could be attributed to the absorption of the stretching vibration of self-associated O-H on the ends of PEA-$(COOH)_2$. This peak shifted to lower wavenumber after PEI was blended because of hydrogen bonding between –COOH on the ends of PEA-$(COOH)_2$ and –NH- on PEI, and the peak was located at 3271 cm^{-1}. The data showed a slight shift by several wavenumbers, but this is reasonable because the original absorption is derived from a hydrogen bonding state of self-associated O-H, not from a free O-H state. The absorption peak at 3382 cm^{-1} on the spectrum of AI-10:1 might come from the stretching vibration of N-H on PEI.

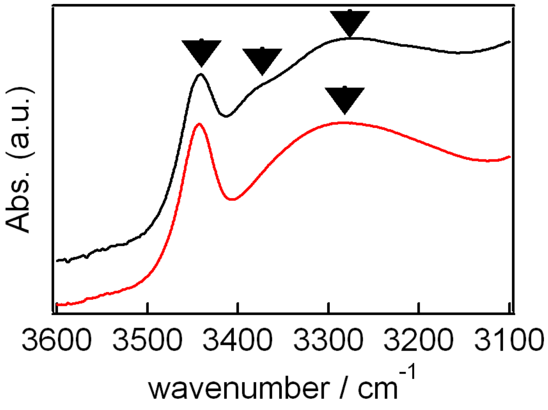


Fig. S3 IR spectra of AI-10:1 (black solid line) and PEA-$(COOH)_2$ (red solid line).

Rheology.

Oscillatory shear measurements were carried out on an ARES-G2 rheometer (TA Instruments.) with 25 mm parallel plates. Dynamic strain sweeps were run to assess the linear viscoelastic regime before each measurement. Dynamic temperature ramp tests of AI-10:1 were run from 45 to 10 °C at a ramp rate of 1 °C/min, a strain of 0.5%, and a frequency of 0.3 rad/s, shown in Fig. 4. Dynamic temperature ramp tests of neat PEA-$(COOH)_2$ were also run from 45 to 10 °C at a ramp rate of 1 °C/min, a strain of 30%, and a frequency of 0.3 rad/s, shown in Fig. 4. Reversibility of the gel was checked by measuring dynamic temperature ramp tests of AI-10:1 upon heating from 10 to 45 °C at a ramp rate of 1 °C/min, a strain of 0.5%, and a frequency of 0.3 rad/s. The data upon heating was almost overlapped with the data upon cooling as shown in Fig. S4, indicating the sample is rheologically-thermoreversible.

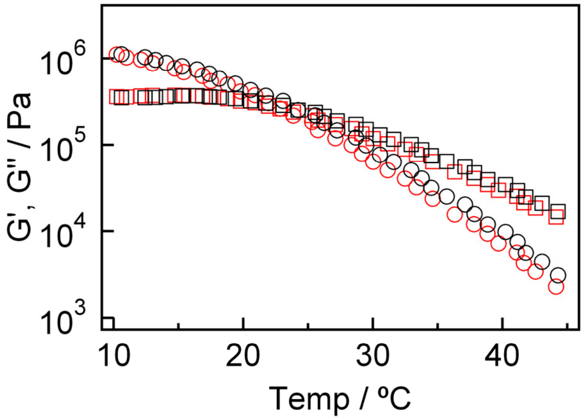


Fig. S4 Elastic moduli (*G'*, ○) and viscous moduli (*G''*,□) of AI-10:1 as a function of temperature at a strain of 0.5 % and a frequency of 0.3 rad/s: red marks for upon cooling; black marks for upon heating.

Dynamic shear moduli for both AI-10:1 and PEA-$(COOH)_2$ in a wide temperature range upon cooling were also shown in Fig. S5 and S6, respectively. A peak on the *G”* curve around -16 °C of Fig. S6 originated from a glass transition temperature (T_g), which was also seen around -1 °C for AI-10:1 as shown in Fig. S5. This is very reasonable because both samples have the same plateau value on *G’* curves under -1 °C for AI-10:1 and -16 °C for PEA-(COOH)$_2$, indicating these plateaus come from the glassy state of poly(ethyl acrylate). DSC data in Fig. S8 and S9 are also consistent with these rheological data.

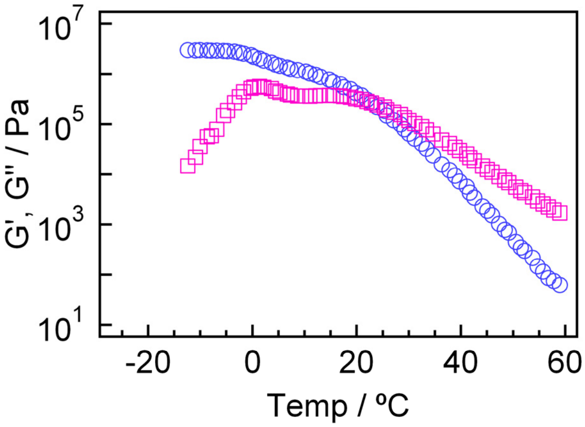


Fig. S5 Dynamic shear moduli of AI-10:1 as a function of temperature at a strain of 0.5 % and a frequency of 0.3 rad/s in a wide temperature range: blue circles for *G’*; pink squares for *G”*.

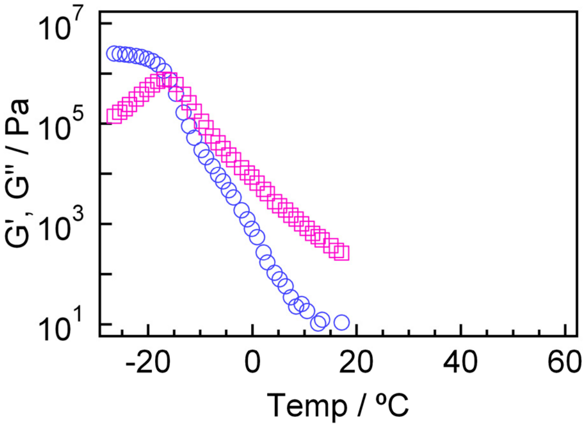


Fig. S6 Dynamic shear moduli of PEA-$(COOH)_2$ as a function of temperature at a strain of 0.5 % and a frequency of 0.3 rad/s in a wide temperature range: blue circles for *G'*; pink squares for *G"*.

Time-temperature superposition master curves for *G'* and *G"* of AI-10:1 with a reference temperature of 30 °C were shown in Fig. S7. The horizontal axis is the reduced frequency ωa_T. At low reduced frequencies, log *G"* has a slope of 2 and log *G'* has a slope of 1, which indicates liquid behavior. The crossover of *G'* and *G"* at approximately 1 rad/s was seen and the longest relaxation time was estimated as approximately 1 s at 30 °C. At higher frequencies, the rubbery plateau of ~ 1 MPa was observed.

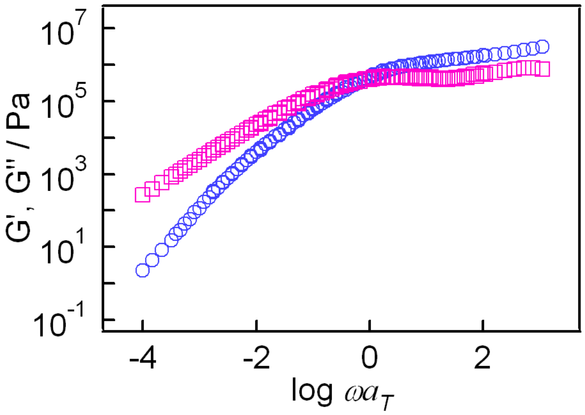


Fig. S7 Elastic moduli (*G'*, ○) and viscous moduli (*G"*,□) of AI-10:1 as a function of reduced frequency at a strain of 0.5 %.

Differential Scanning Calorimetry (DSC).

DSC was used to examine T_gs of polymers. Samples were prepared by sealing approximately 10 mg of samples in aluminum pans. DSC experiments were carried out with EXSTAR DSC 6100

(Seiko Instruments Inc.). An empty hermetic pan was used as the reference in every case. The instrument was calibrated using a melting point of indium (156.6 °C). Nitrogen was used as a purge gas. The temperature ramp rate of 10 °C/min was used for all samples. DSC experiments revealed that AI-10:1, PEA-$(COOH)_2$, and PEI have T_gs at -4.3 °C, -18.7 °C, and -56.9 °C, respectively. This suggests that all samples are melts or liquids which flow at room temperature.

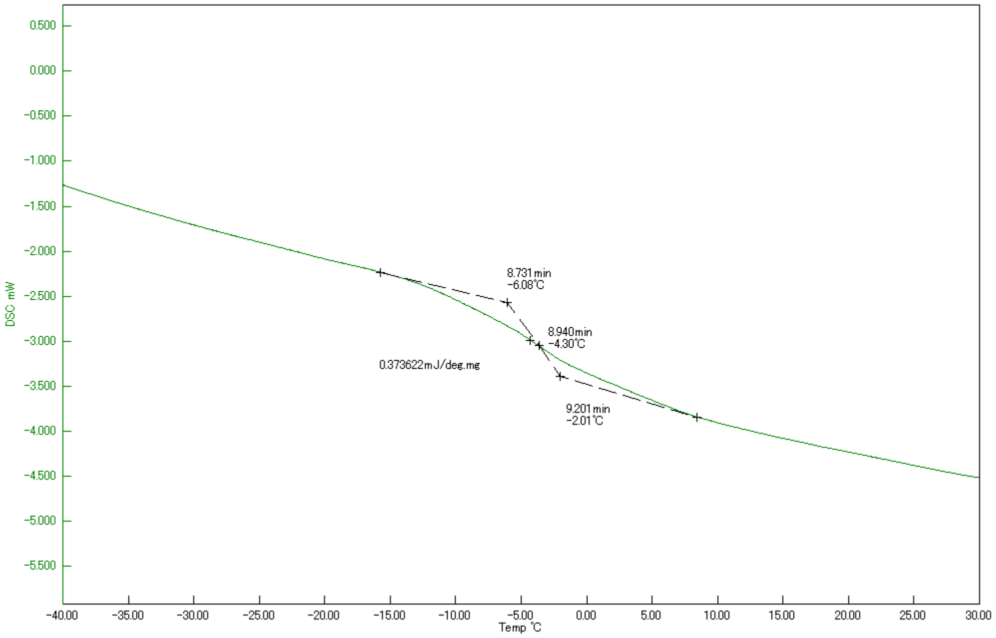


Fig. S8 DSC thermogram of AI-10:1.

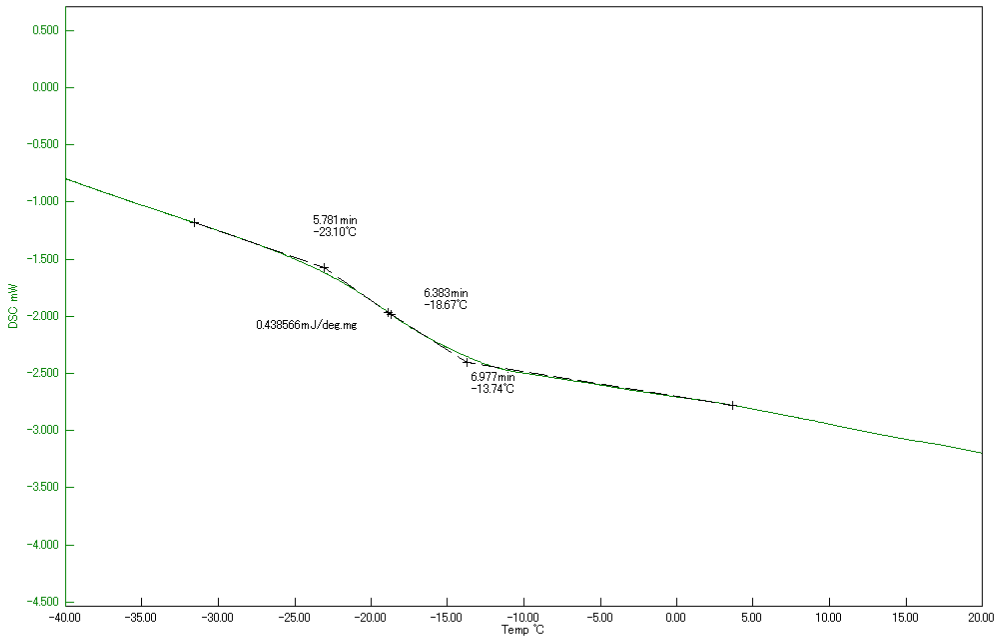


Fig. S9 DSC thermogram of PEA-(COOH)$_2$.

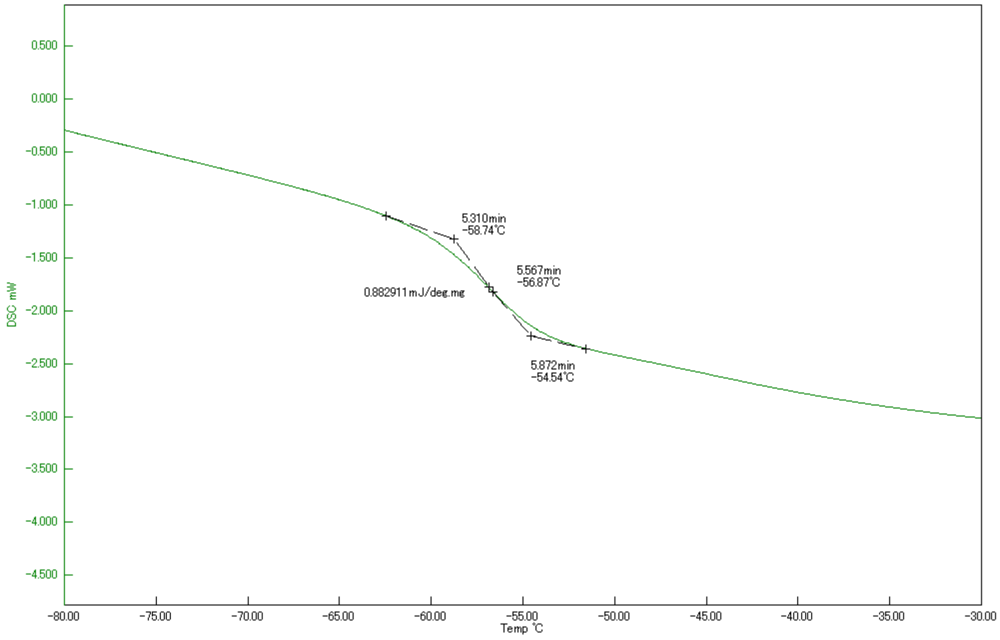


Fig. S10 DSC thermogram of PEI.

SAXS measurements.

Small angle X-ray scattering measurements were carried out to observe the phase separation at nanometer scale with Rigaku NanoViewer. The wavelength of the incident X-ray was 0.1542 nm. The camera length was 735 mm, and imaging plates were used as detectors.

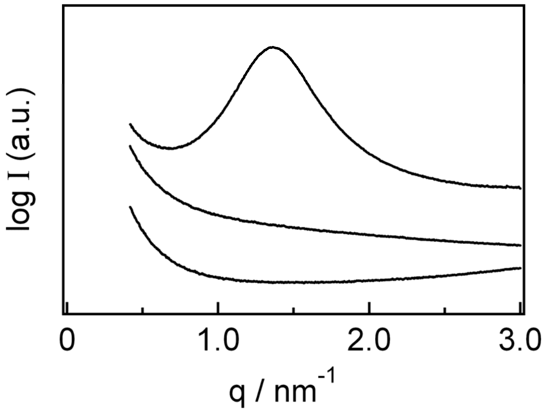


Fig. S11 SAXS profiles of samples: the top for AI-10:1; the middle for PEI; the bottom for PEA-(COOH)$_2$.

Optical images of PDMS-(COOH)$_2$/PEI blends with a higher amount of PEI.

Although supramolecular gels were formed at weight ratios of 10:0.3, 10:0.4, and 10:0.5 for PDMS-(COOH)$_2$/PEI blends, macroscopic phase separation and no gelation were seen for PDMS-(COOH)$_2$/PEI with a higher amount of PEI, such as weight ratios of 10:Z (Z =1, 2, 3, 4, 5) in Fig. S12. Two phases were seen in all vials, where a yellow phase was located at a lower position and a completely cloudy phase was located at an upper position. All of the samples flew easily if the vials were put upside down as in Fig. S13.

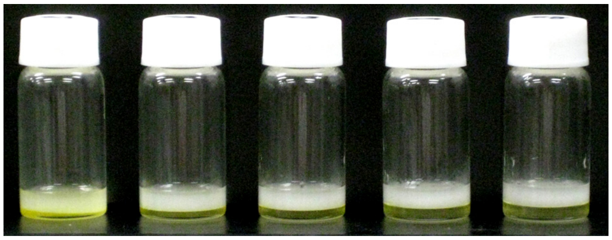


Fig. S12 Optical images of PDMS-$(COOH)_2$/PEI blends with weight ratios of 10:Z (Z =1, 2, 3, 4, 5). The images are displayed in order of the Z value from left to right.

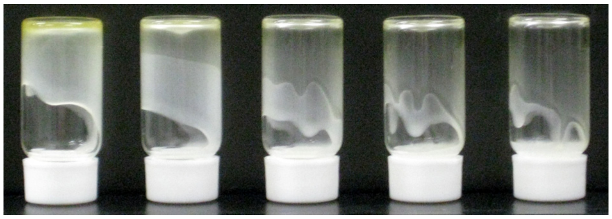


Fig. S13 Optical images of PDMS-$(COOH)_2$/PEI blends with weight ratios of 10:Z (Z =1, 2, 3, 4, 5), where all the vials were placed upside down. The images are displayed in order of the Z value from left to right.

Optical images of PDMS-Me_2/PEI blends.

As control experiment, the methyl-terminated telechelic poly(dimethyl siloxane) (**PDMS-Me_2**, product code: KF-56-50c), which was kindly provided by Shin-Etsu Chemical Co., Ltd, was blended with PEI in THF/MeOH (6:4 by volume). The weight ratios of PDMS-Me_2/PEI were set as 10:0.3 and 10:1.0. There was no color after blend solutions were prepared as in Fig. S14, which are very different from the solutions of PDMS-$(COOH)_2$/PEI blends with a yellow color. Even though solvents in blend solutions of PDMS-Me_2/PEI were removed completely, there was still no color, and a bit cloudy liquids were prepared as in Fig. S15. No gelation has occurred for these PDMS-Me_2/PEI blends, indicating no hydrogen bonding was generated between PDMS-Me_2 and PEI.

Fig. S14 Optical images of approximately 8 wt % PDMS-Me_2/PEI blend solutions with weight ratios of 10:0.3, and 10:1.0. The images are displayed in order of the PEI amount from left to right.

Fig. S15 Optical images of PDMS-$(COOH)_2$/PEI blends with weight ratios of 10:0.3 and 10:1.0, where both vials were placed upside down. The images are displayed in order of the PEI amount from left to right.

UV/visible spectroscopy.

UV/visible spectroscopy of solutions of AI-10:1, PEA-$(COOH)_2$, and PEI was measured at room temperature as shown in Fig. 4c. The optical path length was 5 mm. The instrument used for measurements was UV-VIS spectrometer UV-2550 (Shimadzu, Japan).