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

Atsushi Noro,\* Mikihiro Hayashi, Akihisa Ohshika and Yushu Matsushita\*

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**Preparation of supramolecular polymer gels based on simple molecular design was demonstrated by blending carboxyl-terminated telechelic polymers and poly(ethyleneimine), where balance of an attractive force due to hydrogen bonding and a repulsive force induced by phase separation between polymers has been found as a key factor of supramolecular gelation.**

Polymer gels have been attracting more and more attention as attractive and versatile soft materials. They have been used in our daily lives such as in cosmetics, contact lenses, *etc.*, and are also expected to be developed for high-tech applications.<sup>1</sup> “Supramolecular polymer gels<sup>2,3</sup> (or it could be called supramacromolecular gels)”, as in one category of physical gels, would have three-dimensional transient networks (or supramolecular networks) of polymers at the molecular level, which could be formed by designed building blocks with complementary non-covalent bonding units. Because of the weak association strength at cross-links with a finite lifetime, supramolecular polymer gels exhibit unique features such as self-healing<sup>4</sup> and stimuli-responsiveness<sup>3,5</sup> originated from the network structure.<sup>6,7</sup>

Taking account of two essential components of a bridging strand and a cross-link to build up a supramolecular network of polymers, Meijer and Sijbesma *et al.* prepared supramolecular polymer gels *via* hydrogen bonding from a simple trifunctional copolymer with ureidopyrimidone units on polymer ends.<sup>8</sup> Another tactic to build up supramolecular networks of polymers is to blend two building blocks: a telechelic polymer as a bridging strand and a multifunctional polymer (or oligomer) as a multifunctional cross-linker.<sup>3,5,9</sup> Such a supramolecular network formed by the latter tactics usually contains a large amount of solvents, which is beneficial to producing their unique physical properties; however, the use of solvents lowers the modulus of the gels,<sup>3,10</sup> in other words, resulting in insufficient mechanical strength for applications. If supramolecular polymer gels in bulk with good mechanical properties can be attained by an easy preparation procedure, it is attractive and useful for practical applications of supramolecular polymer gels.

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan. E-mail: yushu@apchem.nagoya-u.ac.jp; noro@nagoya-u.jp; Fax: +81-52-789-3210

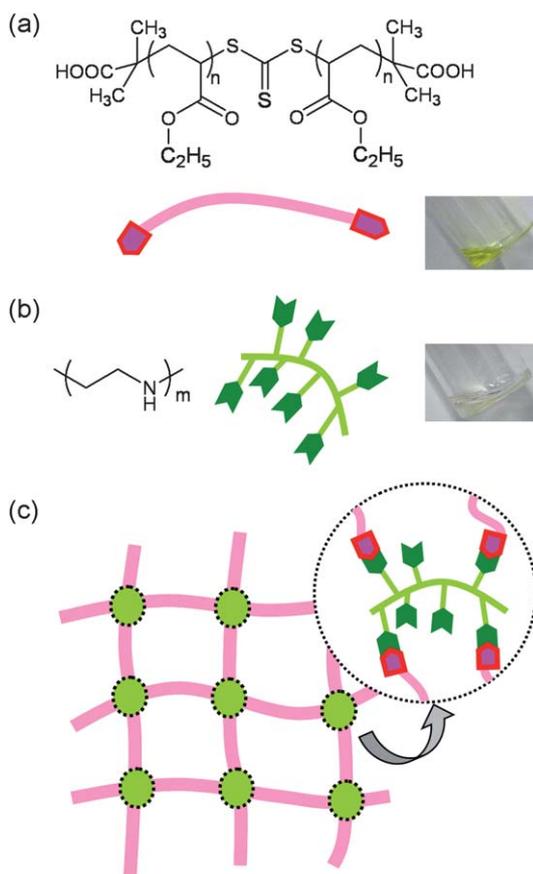
† Electronic supplementary information (ESI) available: Experimental details and additional data of SEC, NMR, IR, rheology, DSC, SAXS, and optical images. See DOI: 10.1039/c0sm01334j

In this communication, we present a preparation procedure of bulk supramolecular polymer gels *via* hydrogen bonding based on simple molecular design, which could possess supramolecular polymer networks at the molecular level as in Fig. 1. To build up supramolecular polymer gels, carboxyl-terminated telechelic poly(ethyl acrylate) (PEA-(COOH)<sub>2</sub>) and poly(ethyleneimine) (PEI) were used as building blocks of a bridging strand and a cross-linker, respectively. PEA-(COOH)<sub>2</sub> was synthesized *via* reversible addition-fragmentation chain transfer (RAFT) polymerization by using the difunctional chain transfer agent with two carboxylic acids, *S,S'*-bis( $\alpha,\alpha'$ -dimethyl- $\alpha'$ -acetic acid)trithiocarbonate (see ESI†).<sup>11</sup> The polydispersity index of the polymer was measured to be around 1.2 by size exclusion chromatography. The number-average molecular weight of PEA-(COOH)<sub>2</sub> was determined to be 9000 by <sup>1</sup>H NMR (Varian) end-group analysis. On the other hand, PEI ( $M_n \approx 1200$ ,  $M_w \approx 1300$ ) was supplied from Aldrich, which is commercially available.

Preparation of supramolecular polymer gels was carried out by blending solutions of the above two polymers, followed by drying the mixture solutions at 50 °C *in vacuo*. A solvent used for solution preparation is a mixed solvent of THF/MeOH (5 : 5 by volume). The weight ratio of PEA-(COOH)<sub>2</sub> : PEI in the blends was varied as 10 : *X*, where five samples with *X* of 0.5, 0.75, 1, 2, and 3 were prepared in total. The blends were coded as AI-10 : *X*.

Fig. 2 displays optical images of all AI-10 : *X* blends. When the *X* value (the amount of PEI) is smaller than unity as AI-10 : 0.5 and AI-10 : 0.75, the samples look like homogeneous liquids and possess fluidity. This is because PEA-(COOH)<sub>2</sub> and PEI have low  $T_g$ s as shown in Fig. 1 ( $T_g(\text{PEA}-(\text{COOH})_2) \approx -19$  °C,  $T_g(\text{PEI}) \approx -57$  °C, see also Fig. S9 and S10†). At the *X* value of unity, however, the blend represents a non-liquid-like state at room temperature, substantially forms a gel, regardless of the fact that both PEA-(COOH)<sub>2</sub> and PEI are liquids at room temperature (see the centre vial in Fig. 2). As the *X* value increases further, the blends still keep a gel state but become cloudy or turbid.

To clarify the origin of gelation behavior of the blends at the molecular level, a FT-IR spectrum was obtained at room temperature as shown in Fig. S3†, which revealed hydrogen bonding between the amine on PEI and the carboxylic acid on both ends of PEA-(COOH)<sub>2</sub>. Needless to state that hydrogen bonding between carboxylic acid and amine plays an essential role for supramolecular gelation in these blends,<sup>12</sup> it must be noted that phase-separation between PEA-(COOH)<sub>2</sub> and PEI also plays an important role for this



**Fig. 1** Schematic illustrations of a model supramolecular network of polymers *via* hydrogen bonding (c) comprised of PEA-(COOH)<sub>2</sub> as pink bridging strands with carboxyl groups at both ends (a) and PEI as green multifunctional cross-linkers with many amino groups (b). Both neat PEA-(COOH)<sub>2</sub> and neat PEI are liquids at room temperature shown as photographs in (a) and (b). PEI could form a spherical cross-link phase by a moderate repulsive force against PEA-(COOH)<sub>2</sub> as shown in (c). This is the most simplified model supramolecular network excluding any other chains and cross-links. Furthermore, possible looping pink PEA chains were also omitted in the supramolecular network for clarity.

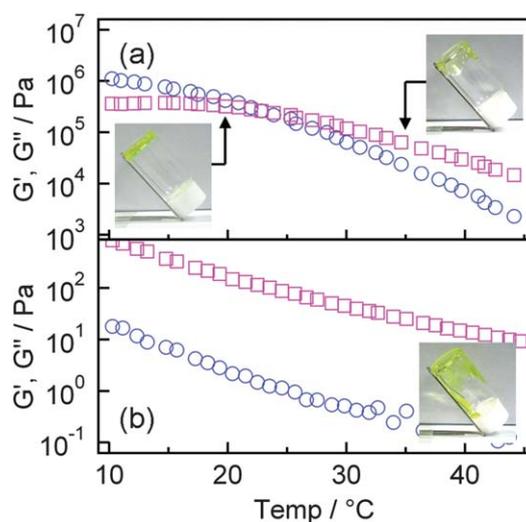
supramolecular gelation, as we clearly recognize phase separation as turbidity in Fig. 2. As is supported in Fig. S11†, small-angle X-ray scattering (SAXS) profiles were compared among AI-10 : 1 and their components, PEA-(COOH)<sub>2</sub> and PEI, at room temperature. AI-10 : 1 shows one broad peak at  $1.3 \text{ nm}^{-1}$ , which cannot be usually seen in immiscible polymer blends, while neat PEA-(COOH)<sub>2</sub> and neat PEI did not show any scattering peaks.<sup>13</sup> This suggests that there exists at least a correlation of electron density between PEA-(COOH)<sub>2</sub> and PEI with the length scale of several nanometres, which might be originated from nanophase-separation between a cross-link phase of PEI and a matrix phase of PEA-(COOH)<sub>2</sub>. This speculation about phase-separation could also be supported by our previous studies on supramolecular polymer gels in an ionic liquid.<sup>3</sup> It can be safely stated that the determinant for this gelation is not only an attractive force of hydrogen bonding but also a repulsive force induced by phase separation. Since the molar amount of amine is much larger (four times larger) than that of carboxylic acid even at liquid-like AI-10 : 0.5, the stoichiometry of a hydrogen bonding pair



**Fig. 2** Optical images of five blends of AI-10 : X ( $X = 0.5, 0.75, 1, 2,$  and  $3$ ). The blends were displayed in the order of  $X$  value from left to right. Gels were not formed at small amount of PEI for  $X = 0.5$  or  $0.75$ . At the optimum amount of PEI ( $X = 1$ ), however, homogeneous and transparent gels were formed. A gel state had been kept up to large amount of PEI ( $X = 2, 3$ ), though the appearance of cloudiness or turbidity is evident.

between carboxylic acid and amine is not regarded as an important factor for this gelation.

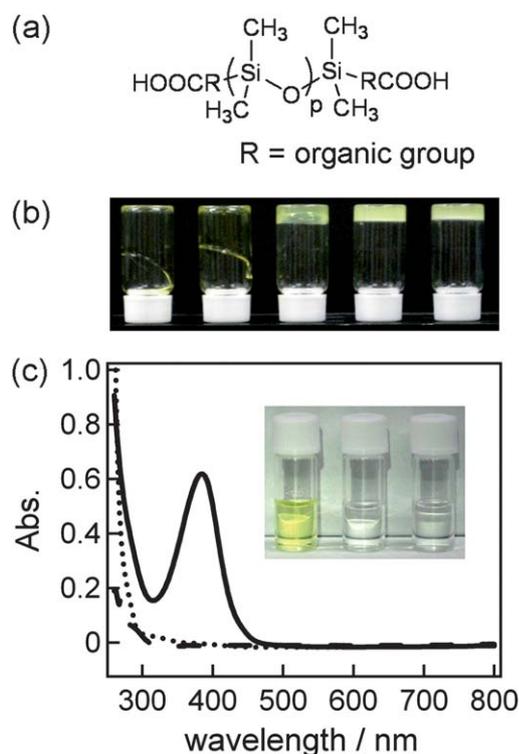
We also investigated the viscoelastic properties of bulk supramolecular polymer gels. Dynamic shear measurements for AI-10 : 1 were carried out on an ARES-G2 rheometer (TA Instruments) by changing the temperature as shown in Fig. 3a. The elastic modulus ( $G'$ ) is less than the viscous modulus ( $G''$ ) at higher temperatures than  $23 \text{ }^\circ\text{C}$ , which indicates liquid-like behavior of the blend in this temperature range (see also an image at the right inset in Fig. 3a); however,  $G'$  has the same value as  $G''$  at  $23 \text{ }^\circ\text{C}$ . Then  $G'$  becomes larger than  $G''$  ( $G' > G''$ ) at lower temperatures and the value of  $G'$  shows approximately 1 MPa (see also an image at the left inset in Fig. 3a). The  $G'$  value of  $\sim 1 \text{ MPa}$  points out that the gel is much more robust against stress than 10 wt% supramolecular polymer gels in solvents (plateau modulus  $G_x \approx 3 \text{ kPa}$ ).<sup>3</sup> The crossover at  $23 \text{ }^\circ\text{C}$  could also be regarded as a gel transition temperature ( $T_{\text{gel}}$ ), which is easily accessible from room temperature, suggesting easy processability. Neat PEA-(COOH)<sub>2</sub> without PEI did not show such



**Fig. 3** Elastic (O) and viscous (□) moduli as a function of temperature at a frequency of  $0.3 \text{ rad s}^{-1}$ : (a) AI-10 : 1 at a strain of 0.5% and (b) neat PEA-(COOH)<sub>2</sub> at a strain of 30%. Temperature ramp tests for both samples were run in the linear viscoelastic regime. The insets are optical images at the corresponding temperatures.

a crossover even at 10 °C, representing liquid behavior in this temperature range as is recognized in the inset of Fig. 3b. The gel of AI-10 : 1 has also been found rheologically thermoreversible by both upon cooling and heating (Fig. S4†), suggesting that the gels were not formed by irreversible chemical bonds but thermoreversible hydrogen bonds between carboxylic acid and amine.

We further examined to prepare supramolecular polymer gels *via* hydrogen bonding by blending two commercially available liquid polymers. Carboxyl-terminated telechelic polydimethylsiloxane (PDMS-(COOH)<sub>2</sub>), which was kindly provided by Shin-Etsu Chemical Co., Ltd. ( $M_n \approx 4600$ , product code: X-22-162C), was blended with PEI in a mixed solvent of THF/MeOH (6 : 4 by volume) by varying the weight ratio of PDMS-(COOH)<sub>2</sub> : PEI as 10 :  $Y$  ( $Y = 0.1, 0.2, 0.3, 0.4,$  and  $0.5$ ), and the blend solutions were dried *in vacuo* at 50 °C. Cloudy gels were formed at  $Y = 0.3, 0.4,$  and  $0.5$  as shown in Fig. 4b probably due to both hydrogen bonding and phase separation. Additionally, blends had a yellow colour, even though the two components, PDMS-(COOH)<sub>2</sub> and PEI, were both almost colourless liquids as displayed in the inset of Fig. 4c. This figure shows a UV-vis spectrum of an 8 wt% solution of the blend with a weight ratio of 10 : 0.1 in THF/MeOH, having an absorption peak at 385 nm with the tail up to 460 nm, which ensures the appearance of a yellow colour. Note the blends of methyl-terminated



**Fig. 4** (a) Chemical structures of PDMS-(COOH)<sub>2</sub>. (b) Optical images of five blends of PDMS-(COOH)<sub>2</sub>/PEI with a weight ratio of 10 :  $Z$  ( $Z = 0.1, 0.2, 0.3, 0.4,$  and  $0.5$ ), which were displayed in order of  $Z$  value from left to right. (c) UV-vis spectra of a PDMS-(COOH)<sub>2</sub>/PEI blend ( $Z = 0.1$ ) solution (solid line), a PDMS-(COOH)<sub>2</sub> solution (dashed line), and a PEI solution (dotted line). The solvent used for measurements was THF/MeOH (6 : 4) and the concentration of solutions was approximately 8 wt%. The instrument used for measurements was a UV-VIS spectrometer UV-2550 (Shimadzu, Japan). The image provided as inset shows solutions of the blend, PDMS-(COOH)<sub>2</sub>, and PEI from left to right.

telechelic polydimethylsiloxane (code: KF-96-50c) and PEI did not form gels nor provide any colour because of no hydrogen bonding formation (see Fig. S14 and S15†). These suggest the yellow colour should be originated from the red shift of the absorption band due to hydrogen bonding between carboxylic acid on each end of the PDMS-(COOH)<sub>2</sub> and many amino groups on PEI even at 10 : 0.1, where the blend was still at a liquid-state. This also indicates that phase separation, which can be easily noticed by turbidity in three blends of PDMS-(COOH)<sub>2</sub>/PEI with  $Z = 0.3, 0.4$  and  $0.5$ , is also another key of supramolecular gelation together with hydrogen bonding.

In conclusion, we have prepared supramolecular polymer gels composed of PEA-(COOH)<sub>2</sub> and PEI *via* hydrogen bonding by a simple preparation procedure. The determinant of this supramolecular gelation is not only hydrogen bonding between two polymers but also a repulsive force induced by phase separation between them, resulting in evident turbidity of solutions at a higher amount of PEI. The modulus of the gel has a much higher value than that of a gel in a solvent, and the  $T_{gel}$  is found around room temperature, both of which indicate good mechanical properties and processability. Blends of two commercially available liquid polymers such as PDMS-(COOH)<sub>2</sub> and PEI also provided cloudy supramolecular gels at a higher amount of PEI, suggesting this preparation procedure should be universal and useful in practical uses.

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