Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Introducing Static Cross-Linking Points into Dynamic Covalent Polymer Gels that Display Freezing-Induced Mechanofluorescence: Enhanced Force Transmission Efficiency and Stability

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Materials

All solvents and reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry and Kanto Chemical, and used as received, unless otherwise noted. 1,4-Dioxane was distilled under reduced pressure over calcium hydride.

Measurements

Variable-temperature electron paramagnetic resonance (EPR) spectroscopy

Variable-temperature EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller.

・BPA-TASN gel n (n: TASN-containing ratio) in 1,4-dioxane (*Q* = 2.8)

The gels swollen with 1,4-dioxane for 2.5 h at 20 °C were contained in 5 mm glass capillaries to be less than 43.5 mm height and the capillaries were sealed after being degassed. The spectra of the 1,4-dioxane gel were measured using a microwave power 0.3 mW and a field modulation of 0.3 mT with a time constant of 0.03 s and a sweep rate of 0.25 mT/s during the cooling process from 25 to −60 °C (25, 20, 15, 10, 5, 0, –5, –10, –15, –20, –25, –30, –35, –40, –45, –50, –55 and –60 °C). The spectra were measured every 5 °C from 25 to 5 °C after waiting for 5 min and from 5 to –60 °C, after waiting for 4 min.

The concentration of the radicals formed from the cleavage of TASN was determined by comparing the area of the observed integral spectrum with a 0.01 mM solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) in the same solvent under the same experimental conditions. In the gel samples, 0.01 mM TEMPOL solution in the same solvent, which was contained in the same size glass capillary to be the same height, was used for the calculation and measured under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard. The concentration of TASN linkages in the gels was calculated by using the gel volume after swelling at r.t. or 20 °C with the assumptions that the density of the cross-linked polymer in the dry state was 1 g/cm^3 and that the composition of the polymer was similar to that of the reaction mixture because the polymer was obtained in quantitative yield.

The g value was calculated according to the following equation:

$$g = h\nu / \beta H$$

where h is the Planck constant, ν is the microwave frequency, β is the Bohr magneton and H is the magnetic field. The equilibrium of TASN was assumed to simply involve the associated TASN and the dissociated radicals, without irreversible side reactions; under this assumption, the ratio of dissociated TASN was calculated from the peak intensity, by using TEMPOL as a standard.

Swelling measurements

Sliced cross-linked polymer was placed in various organic solvents at r.t., and the Q values of the cross-linked polymer were calculated from the weight of the polymer in the dry and gel states. Q is defined as the weight ratio of the amount of absorbed solvent over that of the dry polymer, as follows:

$$Q = (W_{\mathrm{wet}} - W_{\mathrm{dry}}) / W_{\mathrm{dry}}$$

where W_{dry} and W_{wet} are the weights of the dried and wet gels, respectively.

To calculate the concentrations of the gels swollen with various solvents, volume swelling degrees (V/V_0) were measured with the assumptions that density of the cross-linked polymer in the dry state was 1 g/cm^3 and that the composition of the polymer was similar to that of the reaction mixture because the polymer was obtained in quantitative yield. The weight and volume of the cross-linked polymer in gel states were measured by taking the gels out of the solution, removing excess solution from the gel surfaces, weighing, and measuring the dimensions. The gels were kept in darkness during the entire process.

Tensile Tests

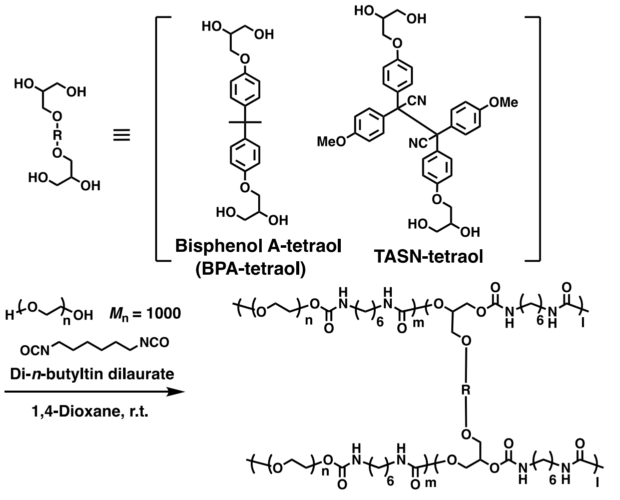
Tensile tests were performed with 100 mm/min elongation rate at r.t. on Shimadzu EZ-L instrument equipped with 50 N load cell.

Dynamic mechanical analysis (DMA)

The viscoelastic properties of **BPA-TASN gel n** were obtained by frequency dispersion measurement in dynamic mechanical analysis (DMA). The measurement was conducted in the shear mode under constant strain and amplitude in the frequency range from 0.1 to 10 Hz at r.t.

Synthesis

Synthesis of BPA-TASN gel n (e.g. n = 50 mol%)



BPA-TASN hybrid-containing cross-linked polyurethane
(BPA-TASN gel n)

Polyethylene glycol (PEG, M_n = 1000) was dried under reduced pressure at 100 °C for 6 hours. A solution of **TASN-tetraol**[1] (0.418 g, 0.670 mmol), **BPA-tetraol**[2] (0.252 g, 0.670 mmol), and PEG (M_n = 1000, 2.68 g, 2.68 mmol) in 1,4-dioxane (4.28 mL) was prepared in a sample tube. Hexamethylene diisocyanate (0.902 g, 5.36 mmol) and a 50 vol % solution of di-*n*-butyltin dilaurate in THF (3 drops) were added to the solution, under a nitrogen atmosphere at r.t. After 48 h, the obtained gel was purified by immersing it in water for 24 h and in 1,4-dioxane for several days and freeze-drying to afford a pale yellow solid (4.25 g, quantitative yield).

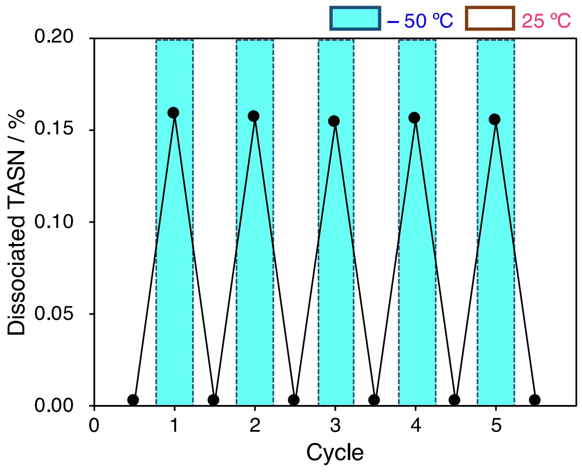


Figure S1. Dissociated TASN (%) in **BPA-TASN gel 25** swollen with 1,4-dioxane (*Q* = 0.79) in response to reversible temperature change cycles (–50 and 25 °C).

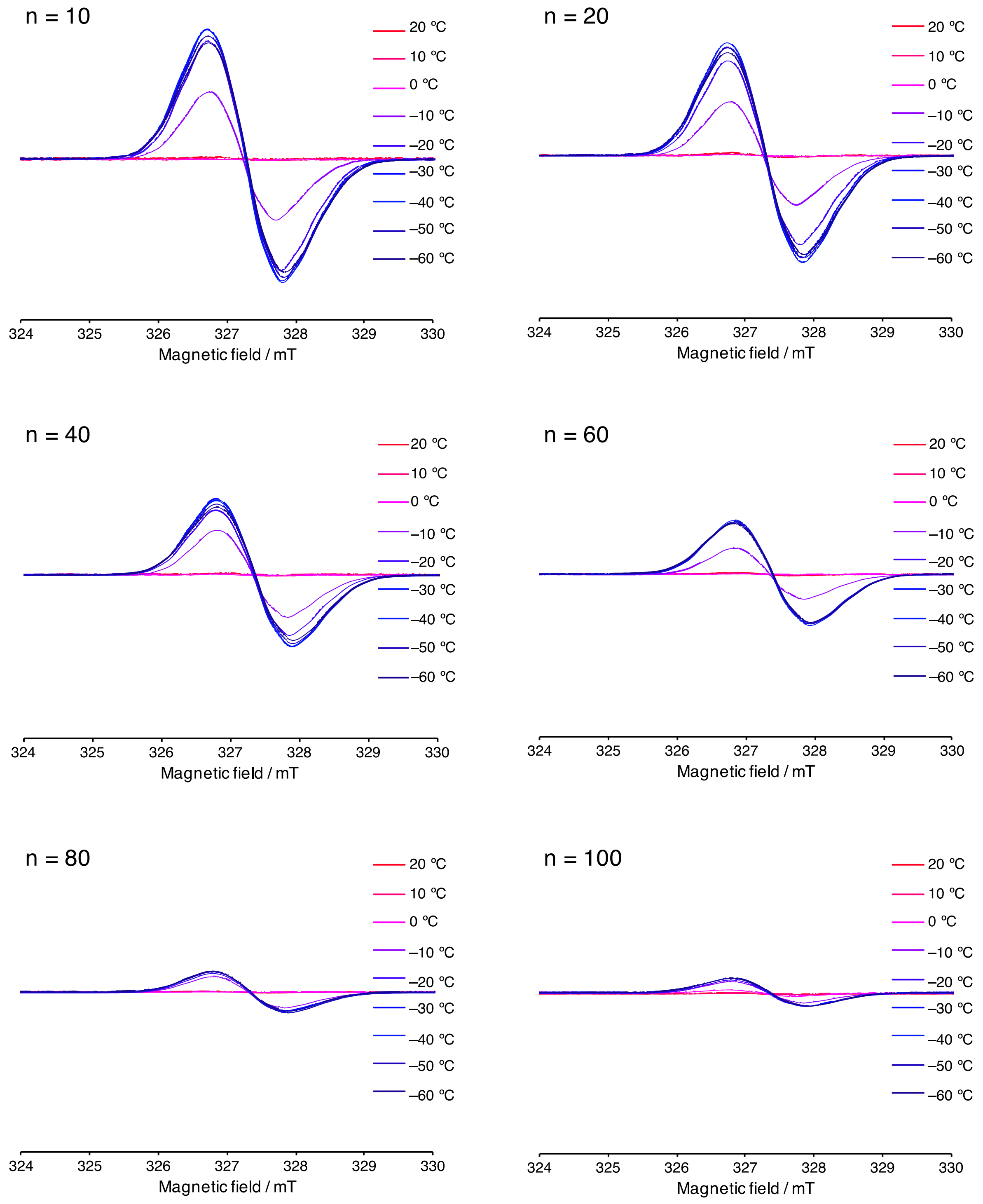


Figure S2. EPR spectra of **BPA-TASN gel n** for each TASN ratio (n = 10, 20, 40, 60, 80 and 100 mol%) swollen with 1,4-dioxane (*Q* = 2.8) at different temperatures (–60 to 25 °C). The integration of the spectra means the percentage of dissociated TASN in Figure 3.

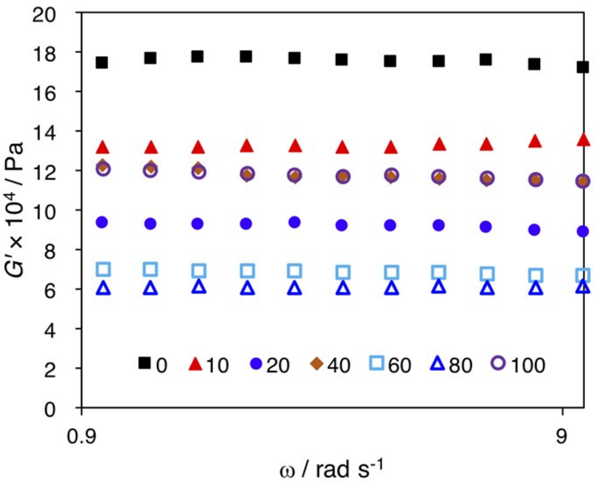


Figure S3. Oscillatory rheology frequency sweeps for **BPA-TASN gel n** (*Q* = 2.8) at each TASN-containing ratio (n = 10, 20, 40, 60, 80, and 100 mol%). Dynamic mechanical analysis (DMA) measurements were performed on **BPA-TASN gel n** (*Q* fixed at 2.8). As a result, it was confirmed that the storage elastic modulus *G′* tends to decrease as the content of the TASN moiety increases. Although dynamic nature of TASN moiety with lower energy of dissociation than that of covalent bond should affect storage elastic modulus, all samples shows relatively good toughness as polymer gels, which can maintain their shape even when the relatively strong mechanical stress was applied.

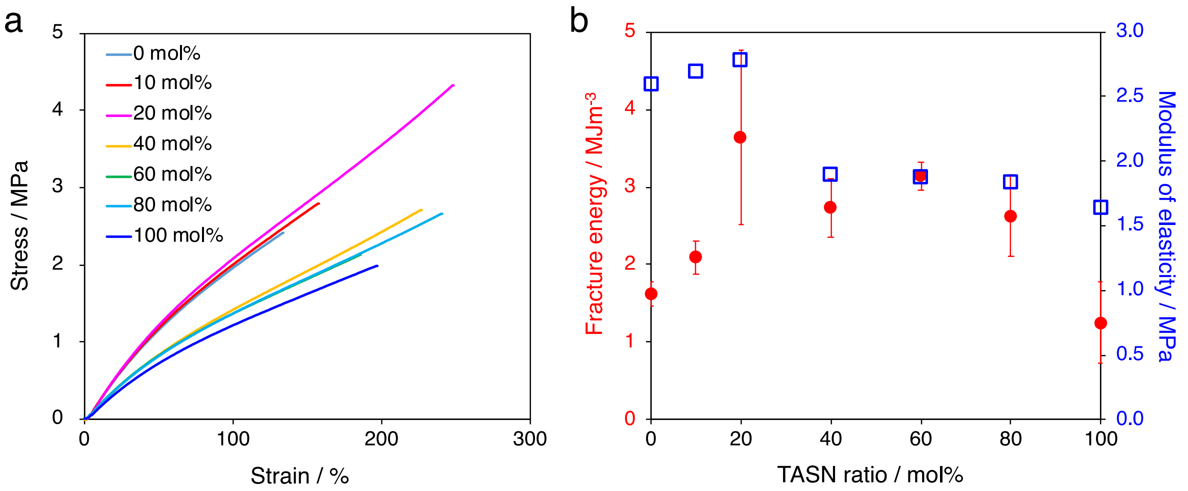


Figure S4. (a) Stress-strain curves of BPA-TASN hybrid-containing cross-linked polyurethane **(BPA-TASN CPU n)** at each TASN-containing ratio (%). (b) Fracture energy (red circle) and modulus of elasticity (blue square). The initial elastic modulus showed a sharp rise from **BPA-TASN CPU 20**, and it was found that the hardness as a material is shown when the static bonds is a majority. Also, the more TASN is introduced as the dynamic bond, the more flexible the material is, it can be confirmed from the decrease of the initial elastic modulus along with the increase of TASN. It was found that **BPA-TASN CPU 20**, in which both the hardness of the static bond and the flexibility as the sacrificial bond of the dynamic bond are combined in a well-balanced manner. It is well extended as the material breaks up to improve the functionality.

References

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(2) Imato, K.; Irie, A.; Kosuge, T.; Ohishi, T.; Nishihara, M.; Takahara, A.; Otsuka, H. *Angew. Chem. Int. Ed.* **2015**, *54* (21), 6168–6172.