

## Electronic Supplementary Information

### **Mechanofluorescent polymer/silsesquioxane composites based on tetraarylsuccinonitrile**

Fumika Hoshino, Takahiro Kosuge, Daisuke Aoki and Hideyuki Otsuka

Department of Chemical Science and Engineering, Tokyo Institute of Technology,  
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

\*Corresponding author: Hideyuki Otsuka (Email: [otsuka@polymer.titech.ac.jp](mailto:otsuka@polymer.titech.ac.jp))

## Materials

Dichloromethane (dehydrated, Kanto Chemical Co., Inc.), (3-isocyanatopropyl)trimethoxysilane (IPTMS) (95%, Gelest, Inc.), di-*n*-butyltin dilaurate (DBTDL) (>95.0%, Tokyo Chemical Industry Co., Ltd.), dibutyltin bis(2,4-pentanedionate) (Sn(*acac*)<sub>2</sub>Bu<sub>2</sub>) (95%, Alfa Aesar), and X-map Type-S (PBA-SiOR) ( $M_n = 24\ 000$ ;  $M_w/M_n = 1.3$ , donated by Kaneka Co.) were used as received without further purification. **TASN-diol** was synthesized according to our previous report.<sup>1</sup>

## Instruments

<sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III HD500 spectrometer. IR spectra were recorded on a JEOL FT/IR-4100 Fourier transform infrared spectrometer as cast on NaCl. Analytical gel permeation chromatographic (GPC) measurements were carried out at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000 and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards ( $M_n = 4430$ – $3242000$ ;  $M_w/M_n = 1.03$ – $1.08$ ) were used to calibrate the GPC system.

## Measurements

### Grinding tests and electron paramagnetic resonance (EPR) spectroscopy

Grinding tests were performed on a Retsch Mixer Mill MM 400. The mechanical force was controlled by vibrational frequency and grinding time. A powdered sample (50 mg) was placed in the grinding jar and ground for 10 min at 30 Hz. The ground sample was transferred into an EPR glass 5 mm capillary and weighted, and the capillary was sealed after being degassed. EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL variable JEOL DVT temperature controller. The spectra of ground samples were measured using a microwave power of 0.08 mW, field modulation of 0.1 mT with a time content of 0.03 s and a sweep rate 0.125 mT s<sup>-1</sup>. The concentration of the radicals formed from cleaved TASN was determined by comparing the area of the observed integral spectrum with that of TEMPOL in benzene under the same experimental conditions. The Mn<sup>2+</sup> signal was used as an auxiliary standard. The *g* value was calculated according to the following equation:  $g = hv/\beta H$  where *h* is the Plank constant, *ν* is the microwave frequency, *β* is the Bohr magneton, and *H* is the magnetic field.

### Tensile tests

Elastic film samples **PBA/TASN-SiO<sub>1.5</sub>-0, 5, 16, 25 and 35** were punched out to dumbbell shaped specimens (JIS K 6251-7, 12 mm × 2 mm × 0.2–0.4 mm). The specimens were stretched in air at r.t.

by using a Shimadzu EZ graph equipped with a 50 N load cell at a crosshead speed of 100 mm min<sup>-1</sup>. The measurements were performed using three pieces for each sample. Fracture energy (*E*) was calculated by the area of the stress-strain curve.

## Synthesis

### Synthesis of TASN-TMS

**TASN-diol** (289 mg, 487 μmol) and **IPTMS** (233 μL, 1.22 mmol) were dissolved in dry dichloromethane (1.40 mL) under a nitrogen atmosphere in a Schlenk tube, followed by adding 104 μL of **DBTDL** (76.1 μL) solution in dichloromethane (1.00 mL). The reaction mixture was allowed to stand at 35 °C for 1.5 hours. The reaction mixture was without purification to prevent condensation of trimethoxysilyl groups in the purification process. The reaction was evaluated by GPC, FT-IR and <sup>1</sup>H NMR measurements.

### Synthesis of TASN-SiO<sub>1.5</sub>

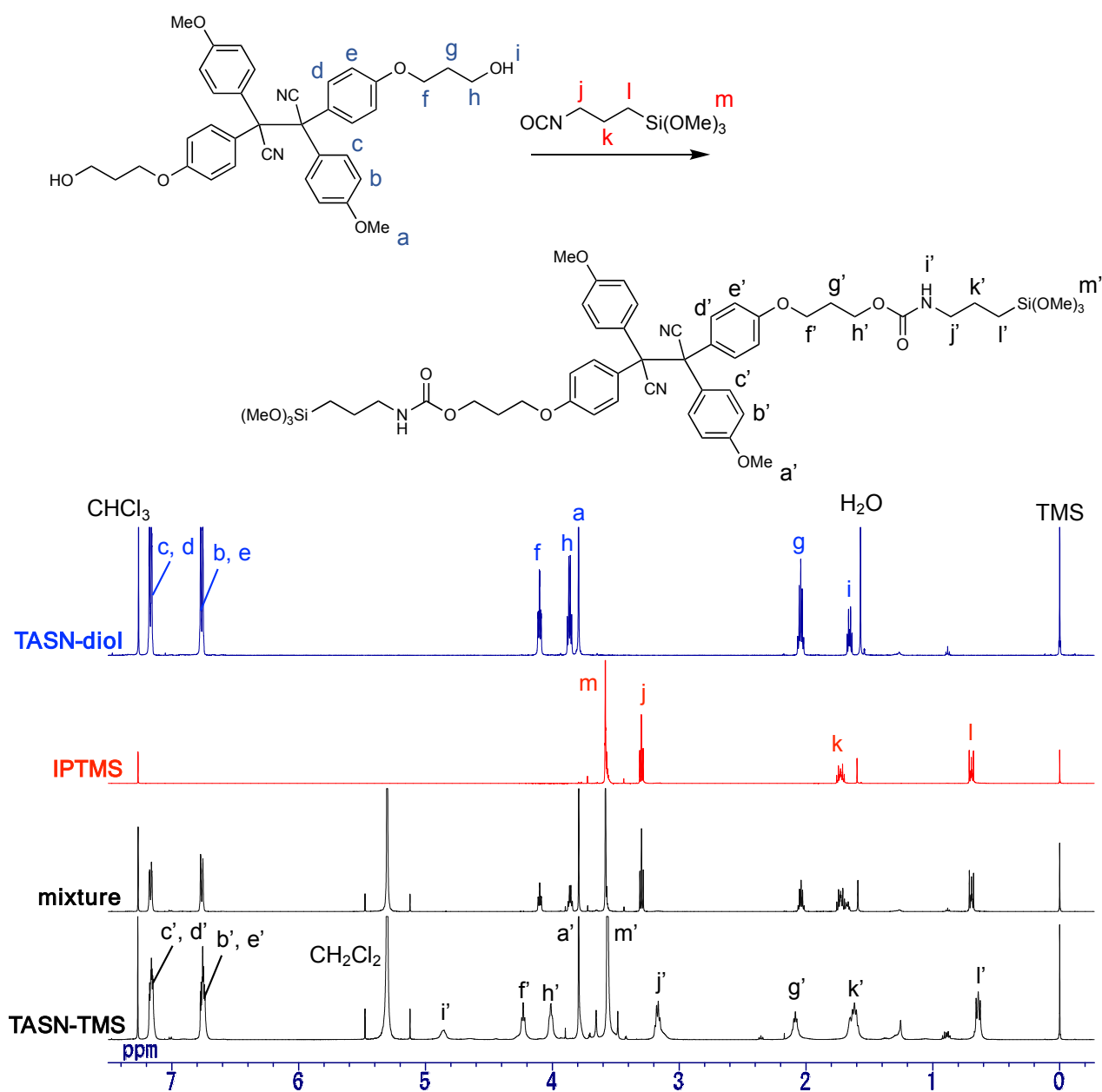
Two drops of **Sn(acac)<sub>2</sub>Bu<sub>2</sub>** were added to the **TASN-TMS** solution synthesized at preceding paragraph. Then, the mixture was poured into a PFA square Petri dish (20 mm × 20 mm, square) and stood still for 1 week in air at r.t.

### Synthesis of composites of TASN-TMS and PBA-SiOR (In a typical preparation of PBA/TASN-SiO<sub>1.5</sub>-35)

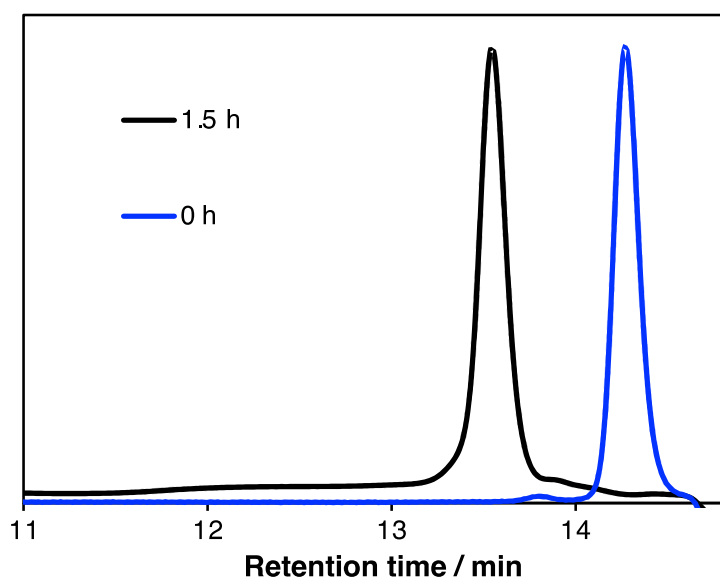
A solution of **TASN-TMS** prepared from 289 mg of **TASN-diol** was added to a solution of **PBA-SiOR** (1.00 g) in dichloromethane (1.00 mL), and two drops of **Sn(acac)<sub>2</sub>Bu<sub>2</sub>** were added to the mixture. Then the resulting mixture was poured into a PFA Petri dish (ϕ 50 mm), cured for 1 weeks in the air at r.t.

**Table S1.** Weight ratio of **PBA-SiOR** and **TASN-TMS** for synthesis of **PBA/TASN-SiO<sub>1.5</sub>-0, 5, 16, 25, 35 and 65**.

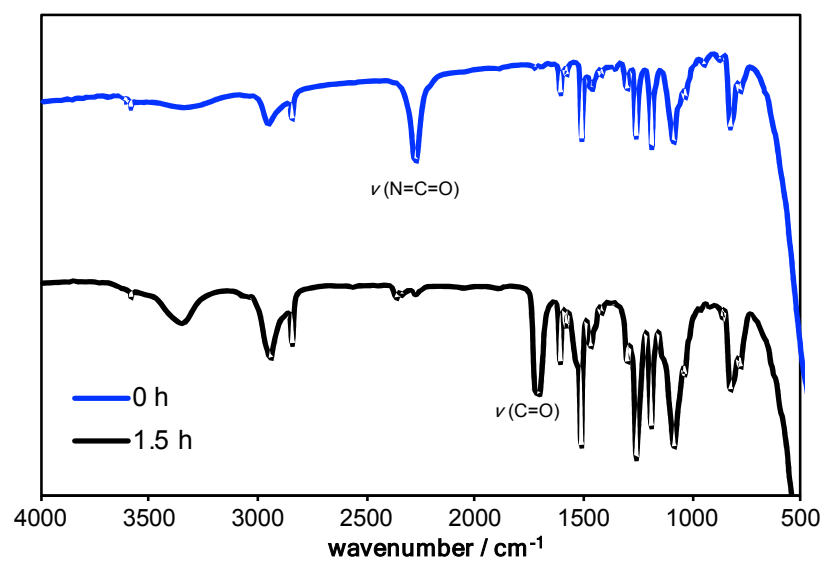
<b>PBA/TASN-SiO<sub>2</sub>-x</b>	<b>x = 0</b>	<b>5</b>	<b>16</b>	<b>25</b>	<b>35</b>	<b>65</b>
<b>PBA-SiOR content (wt %)</b>	100	95	84	75	65	35
<b>TASN-TMS content (wt %)</b>	0	5	16	25	35	65



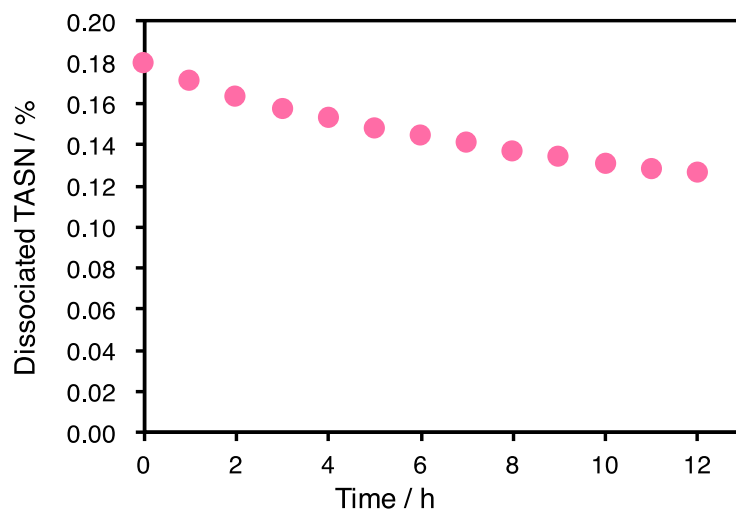
**Figure S1.** <sup>1</sup>H NMR spectra of **TASN-diol** (green), **IPTMS** (blue), **TASN-diol** and **IPTMS** mixture before adding **DBTDL** (red) and the obtained solution of **TASN-TMS** (black).



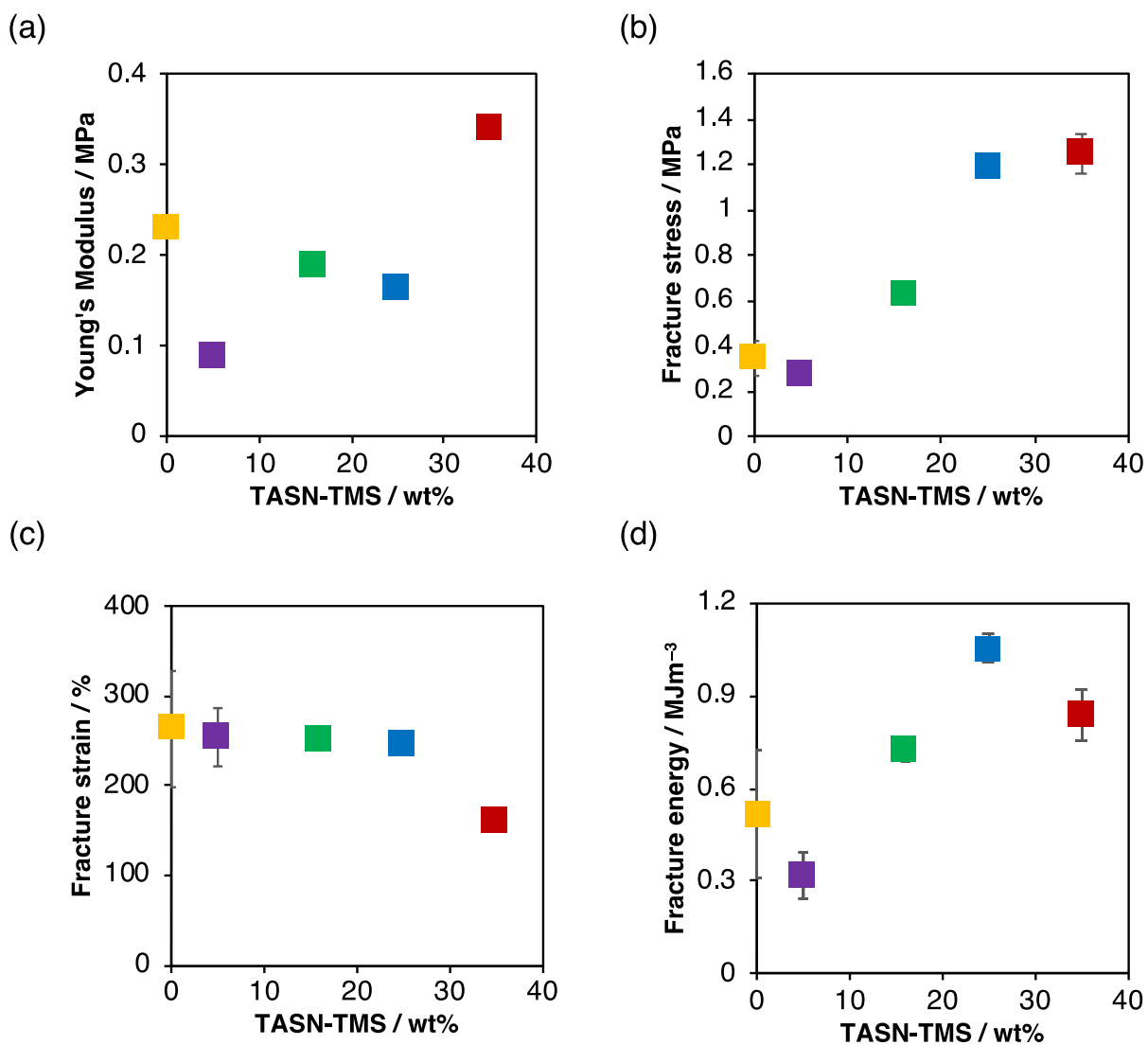
**Figure S2.** GPC curves of the obtained solution of TASN-diol and IPTMS mixture before adding DBTDL (blue) and after 1.5 h (black).



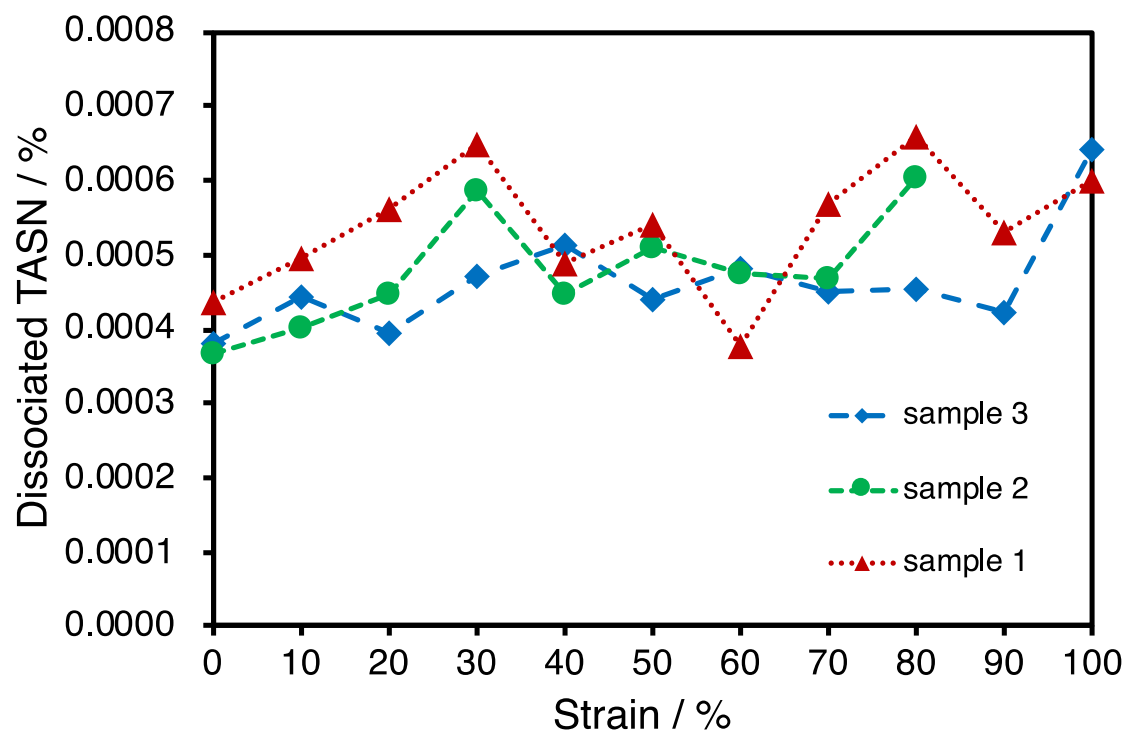
**Figure S3.** FT-IR spectra of the obtained solution of **TASN-diol** and IPTMS mixture before adding DBTDL (blue) and after 1.5 h (black).



**Figure S4.** Radical intensity transitions in EPR measurements after grinding **TASN-SiO<sub>1.5</sub>** under vacuum.



**Figure S5.** Plots of (a) Young's modulus, (b) Fracture stress, (c) Fracture strain, and (d) Fracture energy versus weight content of **TASN-TMS** in composites **PBA/TASN-SiO<sub>1.5</sub>-x**.



**Figure S6.** Dissociated ratios of TASN mechanophores in PBA/TASN-SiO<sub>1.5</sub>-25 during stretching.

## Reference

- 1 T. Sumi, R. Goseki and H. Otsuka, Tetraarylsuccinonitriles as mechanochromophores to generate highly stable luminescent carbon-centered radicals, *Chem. Commun.*, 2017, **53**, 11885–11888.