Supplementary Information

Visualization of mechanochemical polymer-chain scission in double-network elastomers using a radical-transfer-type fluorescent molecular probe

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1. Materials

All solvents and reagents were purchased from Tokyo Chemical Industry, Wako Pure Chemical Industries, Kanto Chemical, and Sigma-Aldrich and used as received, unless otherwise noted. **DAAN** was synthesized according to a previously published method.[1] Methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and triethylene glycol dimethacrylate were passed through a column of basic alumina to remove the inhibitor.

2. Instrument

DSC measurements were carried out using a SHIMADZU DSC-60A Plus with a heating rate of 10 °C/min. UV curing (365 nm wavelength) was performed with a UV-LED light source, CCS HLDL-120U6-NWPSC. Tensile tests were performed on a SHIMADZU EZ-L instrument equipped with a 100 N load cell at room temperature. The films were punched out into dog-bone-shaped pieces standardized as JIS-7 (12 mm × 2 mm gauge section) with a thickness of 0.62–0.78 mm. Fluorescence measurements were carried out using a spectrofluorometer (JASCO FP-8550) between 500 and 750 nm.

3. Synthesis of Double-network Elastomers

3.1. Synthesis of FNs

A typical procedure for the preparation of SNs is described as follows. A solution of EA (15.0 g, 150 mmol) and triethylene glycol dimethacrylate (1.29 g, 4.50 mmol) in dehydrated DMAc (15.1 g, ca. 50 wt%) was degassed with three freeze-pump-thaw cycles. Following the addition of V-70 (173 mg, 0.749 mmol), the resulting solution was again degassed with a freeze-pump-thaw cycle. After vigorous stirring, the homogeneous solution was transferred via syringe to a 0.5 mm thick glass mold placed in an N_2-filled separable flask, which was left at r.t. for 2 days. The obtained polymer network was washed with mixed solvents of chloroform/methanol several times. The washed film was adequately shrunk by immersion into methanol, followed by drying in air at r.t. for a day. The resulting film was dried in vacuo for a day at 40 °C to afford EA-3 as a colorless film (15.3 g, 93.7% yield).

3.2. Synthesis of DNs

Pieces of FNs were immersed into a monomer bath composed of MA (240 g, 2.79 mol), which was purged with nitrogen for 30 minutes before use, triethylene glycol dimethacrylate (7.98 g, 27.9 mmol), and 1-hydroxycyclohexyl-phenyl ketone, known as Irgacure 184 (1.42 g, 6.97 mmol). After swelling to their equilibrium state, which took about 3 h, the resulting gels were sandwiched by Naflon tapes and placed between two Petri dishes. The whole sample holder was exposed to UV for 6.7 min (10 sec × 10, 5 min × 1) with careful attention to excess heat of polymerization. After being left to stand for a day, the cured films were washed with mixed solvents of chloroform/methanol several times. The washed films were adequately shrunk by immersion into methanol, followed by air-drying at r.t. for a day. The resulting films were dried in vacuo for a day at 40 °C to afford DNs as colorless films. Synthesis and characterization of DNs are summarized in **Table S1**.

Table S1. Synthetic results of multi-network elastomers

	Yield [%]		Q^a [-]	$\chi_{FN}{}^b$ [%]	$T_g{}^c$ [°C]	
	FN	DN			FN	DN
EA-1/MA	90.5	98.4	6.64	13.1	–20.88	–4.02
EA-2/MA	90.6	98.1	6.24	13.8	–17.21	–9.83
EA-3/MA	93.7	98.7	4.64	17.7	–14.58	–3.46
BAEA-3/MA	85.1	99.1	5.16	16.3	–33.42	2.53
BA-3/MA	85.8	97.6	5.36	15.7	–49.23	6.64

[a]Swelling degree of the precursor polymer network in the monomer solution. [b]Weight fraction of the FN. [c]Glass transition temperature determined by DSC.

The swelling degree, Q, in the monomer solution was calculated using eq 1.

$$Q = \frac{W_{wet} - W_{dry}}{W_{dry}} \#(1)$$

Here, W_{dry} and W_{wet} refer to the weight of the pristine and swollen elastomers, respectively. The results showed that as the crosslink density increased, the Q decreased and weight fraction of the FN, χ_{FN}, increased. On the other hand, as FN became more flexible, the Q increased and χ_{FN}, decreased.

4. Experimental Data

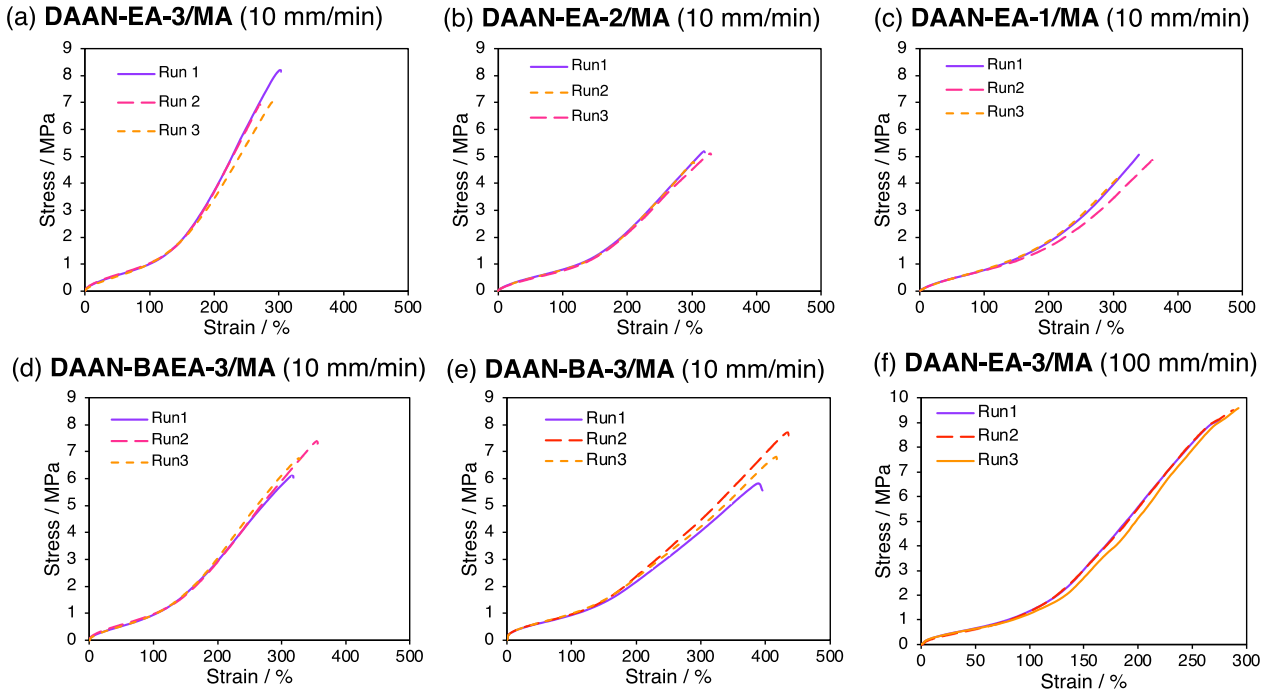

Figure S2. Stress-strain curves of a) **DAAN-EA-3/MA** (10 mm/min), b) **DAAN-EA-2/MA** (10 mm/min), c) **DAAN-EA-1/MA** (10 mm/min), d) **DAAN-BAEA-3/MA** (10 mm/min), e) **DAAN-BA-3/MA** (10 mm/min), and f) **DAAN-EA-3/MA** (100 mm/min).

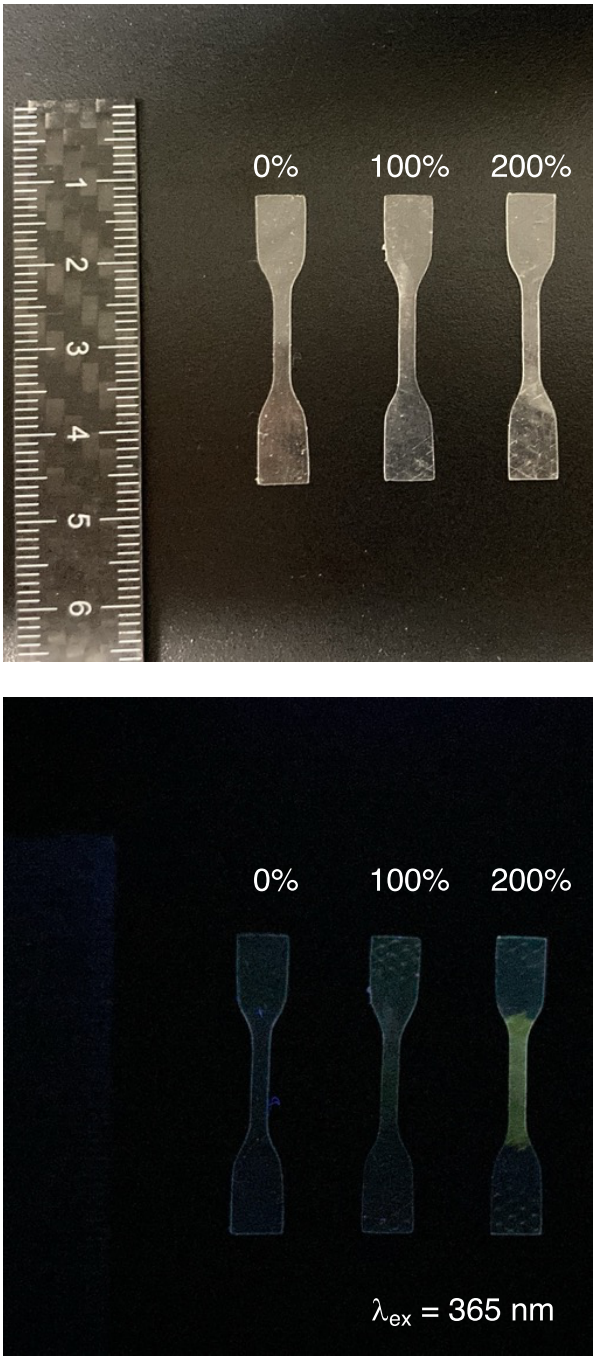

Figure S2. Photographs of **DAAN-EA-3/MA** before and after tensile tests (10 mm/min) under visible light (top) and UV (λ_{ex} = 365 nm) irradiation (bottom).

The original fluorescence intensity values at each strain were obtained as the mean values of the intensity component in the specimen area using ImageJ software. The obtained values were then corrected to account for Poisson's ratio = 0.5 (the original fluorescence intensity can be found in Figure S3).

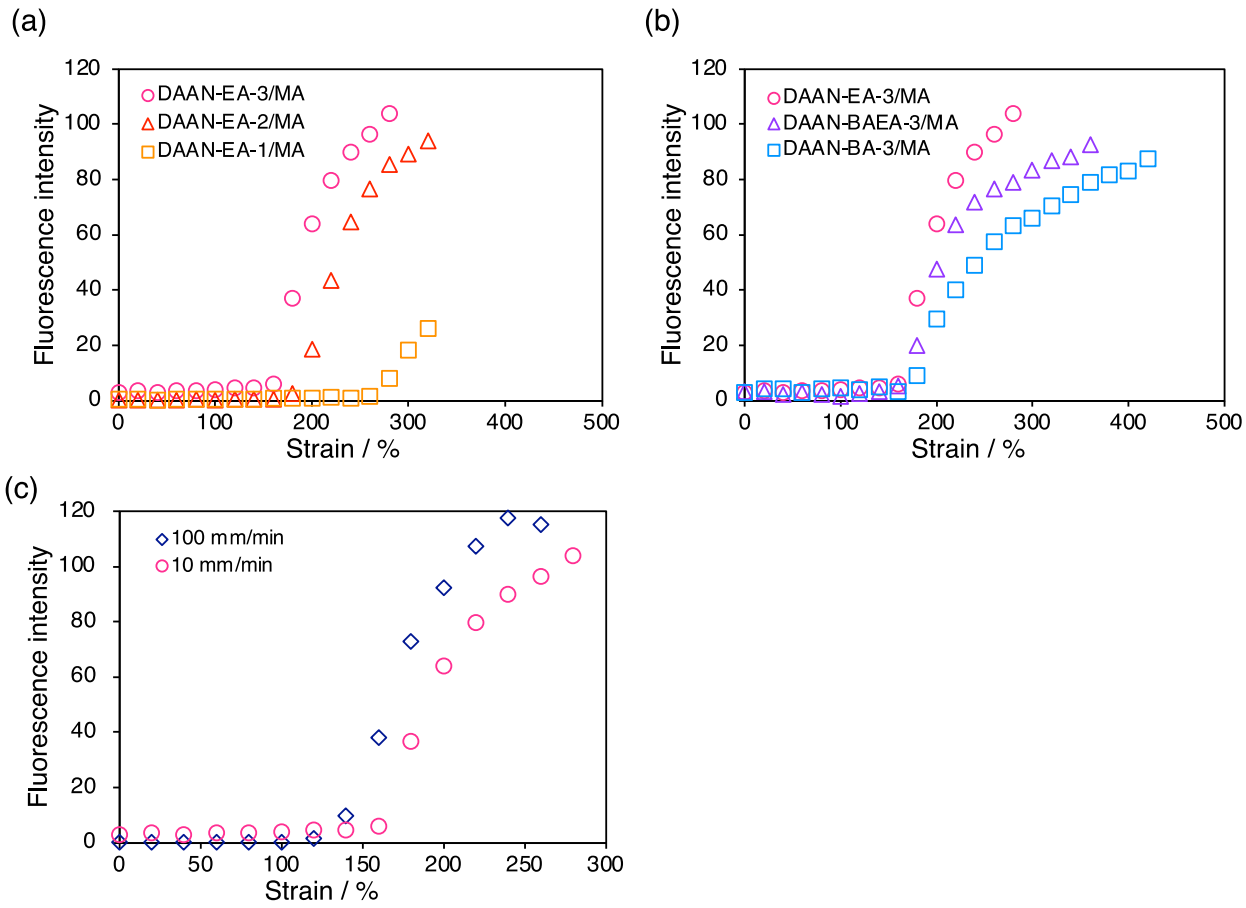

Figure S3. Original fluorescence intensity of (a) **DAAN-EA-3/MA** (10 mm/min)**, DAAN-EA-2/MA** (10 mm/min), and **DAAN-EA-1/MA** (10 mm/min), (b) **DAAN-EA-3/MA** (10 mm/min), **DAAN-BAEA-3/MA** (10 mm/min), and **DAAN-BA-3/MA** (10 mm/min), and (c) **DAAN-EA-3/MA** (100 mm/min) and **DAAN-EA-3/MA** (10 mm/min).

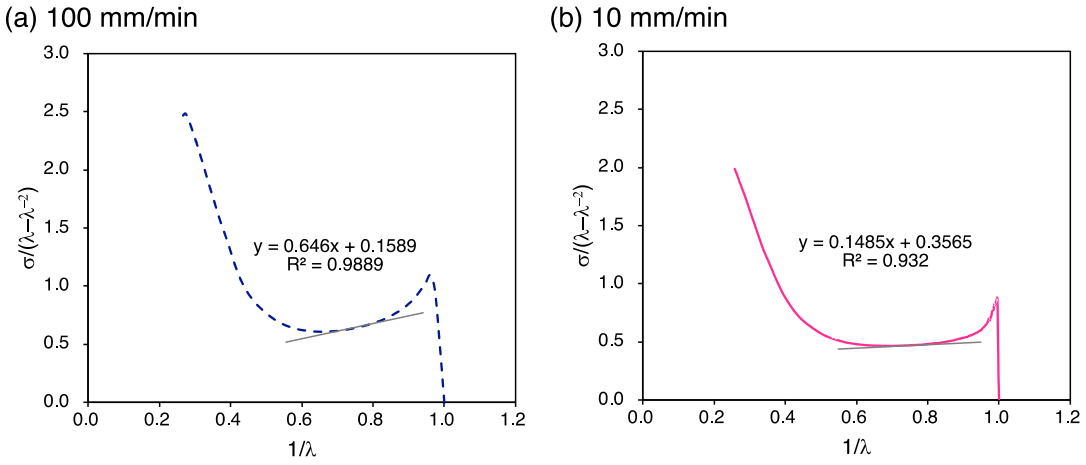

Figure S4. Mooney-Rivlin plots of (a) **DAAN-EA-3/MA** (100 mm/min), (b) **DAAN-EA-3/MA** (10 mm/min).

Table S2. Mooney-Rivlin constants of **DAAN-EA-3/MA**

Tensile speed / mm min^{-1}	C_1 / MPa	C_2 / MPa
10	0.178	0.0743
100	0.0795	0.323

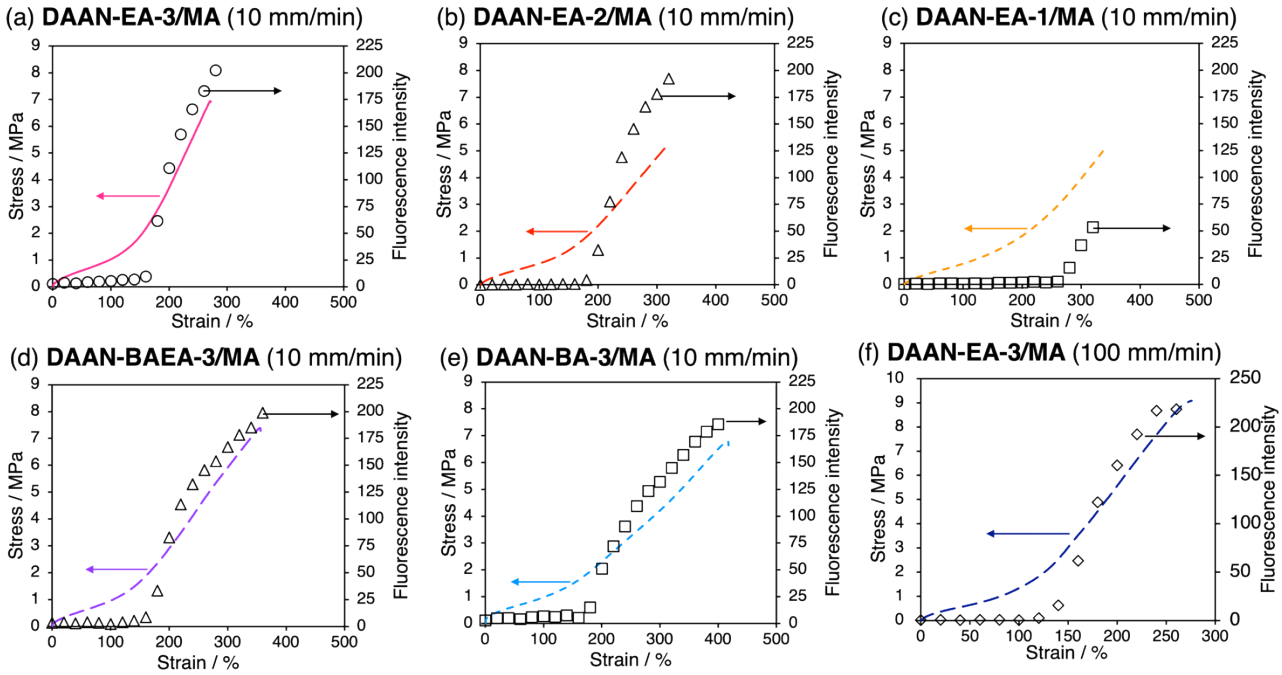

Figure S5. Overlay of stress-strain curves with plots of fluorescence intensity of a) **DAAN-EA-3/MA** (10 mm/min), b) **DAAN-EA-2/MA** (10 mm/min), c) **DAAN-EA-1/MA** (10 mm/min), d) **DAAN-BAEA-3/MA** (10 mm/min), e) **DAAN-BA-3/MA** (10 mm/min), and f) **DAAN-EA-3/MA** (100 mm/min).

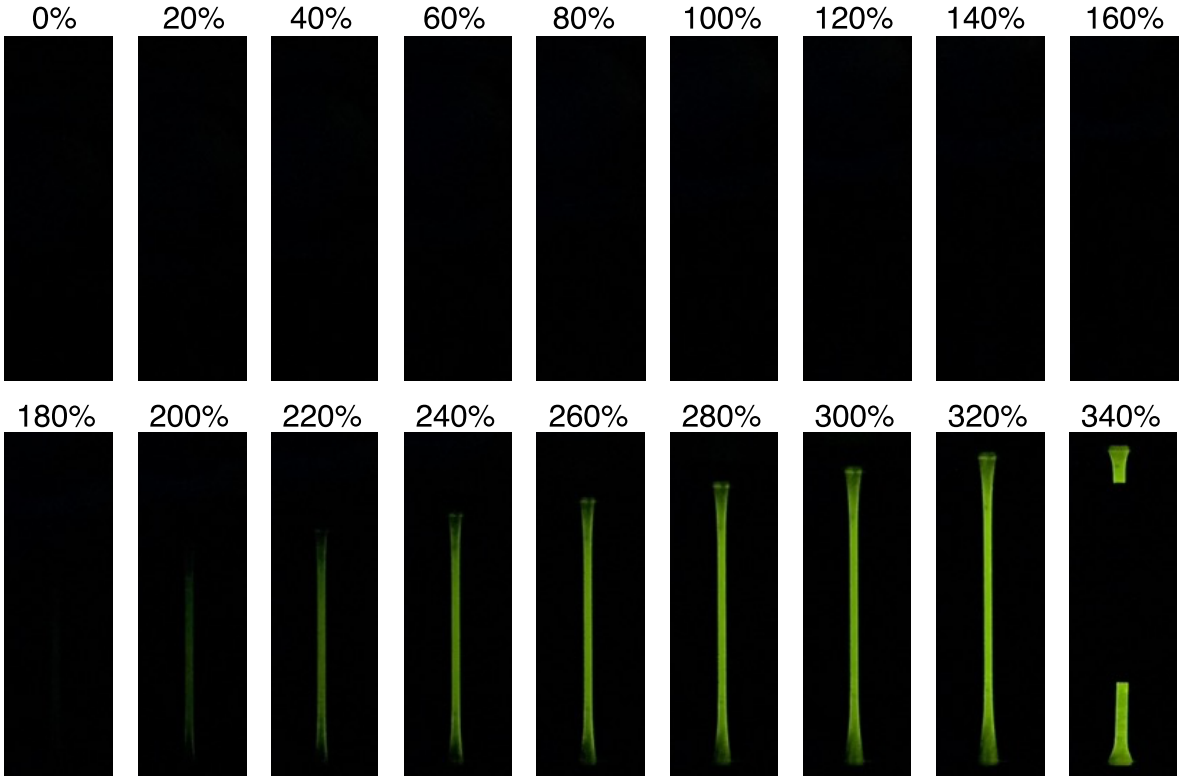

Figure S6. Digital images of **DAAN-EA-2/MA** during stretching (10 mm/min) used for a fluorescent intensity analysis.

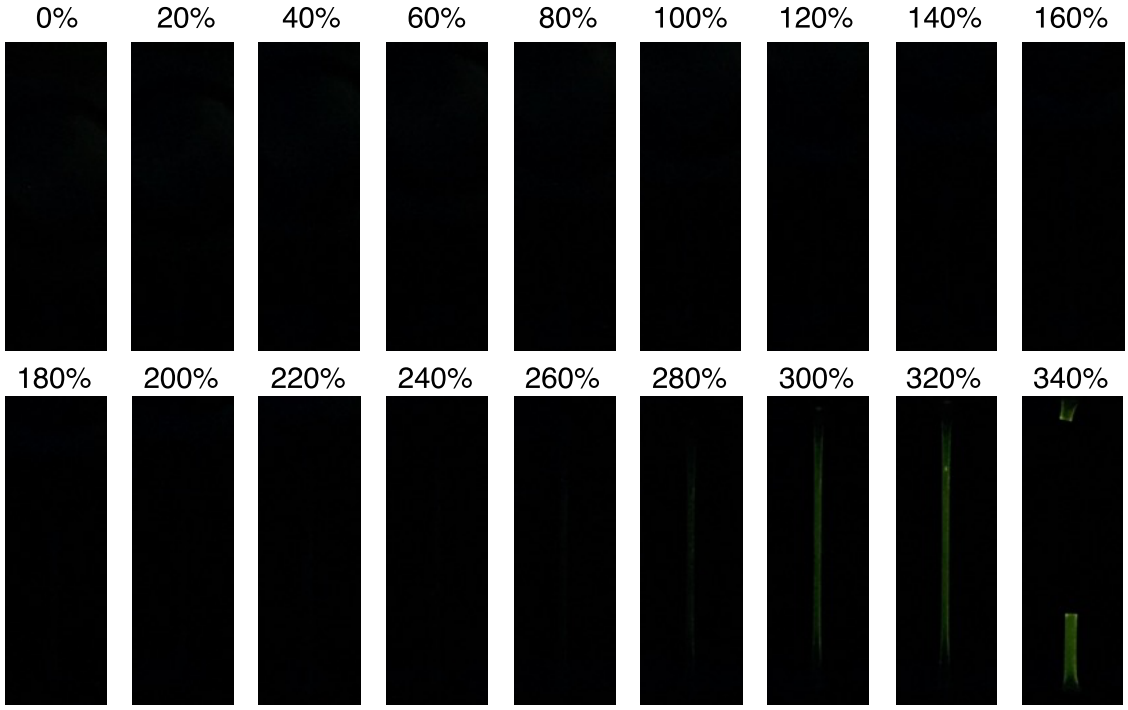

Figure S7. Digital images of **DAAN-EA-1/MA** during stretching (10 mm/min) used for a fluorescent intensity analysis.

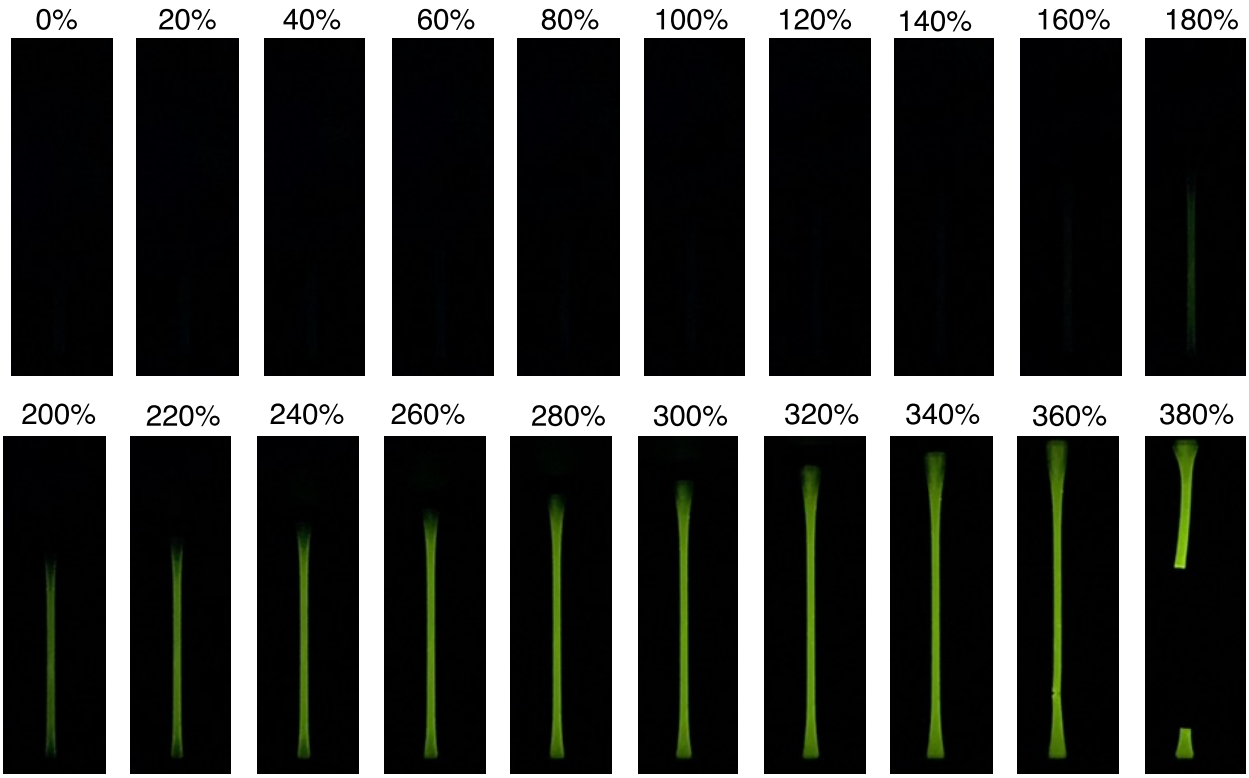

Figure S8. Digital images of **DAAN-BAEA-3/MA** during stretching (10 mm/min) used for a fluorescent intensity analysis.

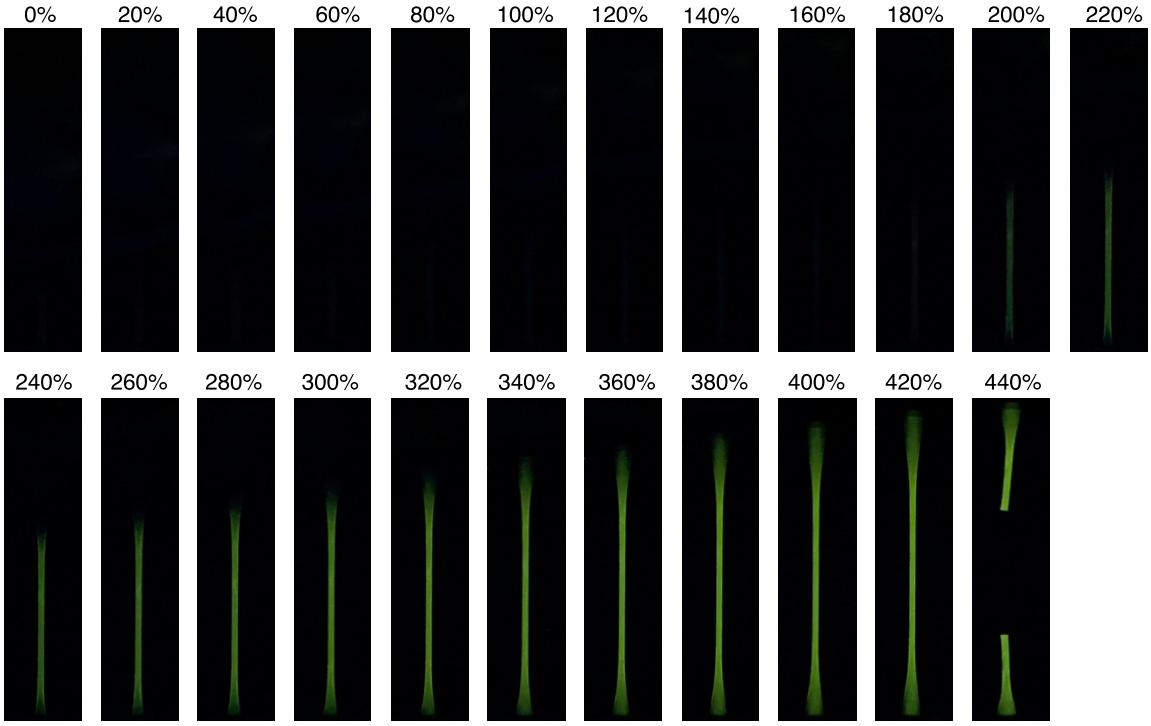

Figure S9. Digital images of **DAAN-BA-3/MA** during stretching (10 mm/min) used for a fluorescent intensity analysis.

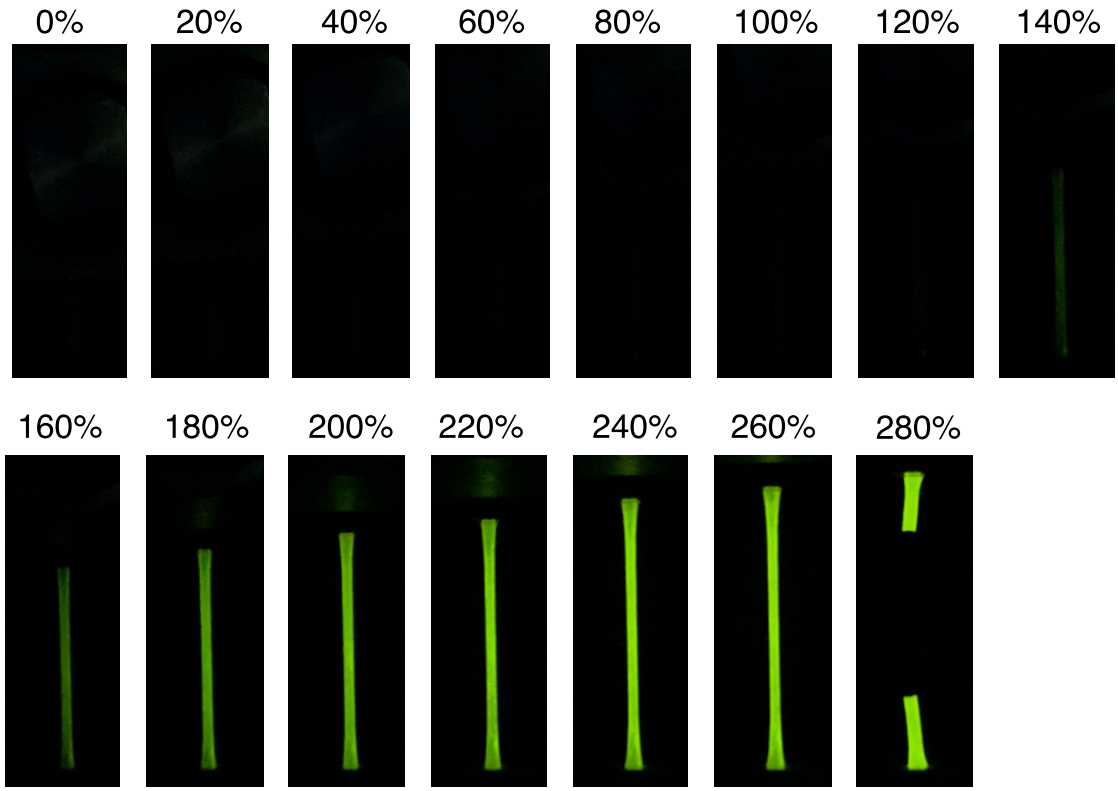

Figure S10. Digital images of **DAAN-BA-3/MA** during stretching (100 mm/min) used for a fluorescent intensity analysis.

Reference

(1) Yamamoto, T.; Otsuka, H.Efficient detection of polymeric mechanoradicals via fluorescent molecular probes stabilized by steric hindrance *Polym. Chem.* **2023**, *14* (20), 2464–2468.