Supporting Information

Highly contrastive, real-time modulation of light intensity by reversible stress-whitening of spontaneously formed nanocomposites: Application to wearable strain sensors

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Experimental

Materials

Diethoxydimethylsilane, diethoxymethylvinylsilane, and diethoxymethylsilane were acquired from Tokyo Chemical Industry Co., Ltd. *tert*-Butyl acrylate (*t*BA), 37 % hydrochloric acid (HCl), platinum (0)-1,3-divinyl-1,1,3,3,-tetramethyldisiloxane complex solution containing 0.05 mol% of platinum, 2,2-dimethoxy-2-phenylacetophenone, and chloroform-d_1 were purchased from Aldrich Chemical Co., Inc. Magnesium sulfate and ethyl acetate (EA) were acquired from Junsei Chemical Co., Ltd.

Synthesis of poly(dimethylsiloxane-co-methylsiloxane) (PDMMS)

50.1 g of diethoxydimethylsilane, 5.0 g of diethoxymethylsilane, 5.7 mL of distilled water, and 1.5 mL of 37 % HCl were used. The feeding mole ratio of diethoxydimethylsilane to diethoxymethylsilane is 0.90 to 0.10. The detailed polymerization and purification methods can be found in our previous report. Yield: 22.3 g (82 %). M_n=6.0×10^3 g/mol. M_w=18.4×10^3 g/mol. n:o (mole ratio)=0.900:0.100. IR ν_{max} (cm^{-1}): 2963s, 2905m (C-H str., methyl); 2156m (Si-H str.); 1412m (C-H ben., methyl); 1093s, 1023s (Si-O-Si str.). ^{1}H NMR δ_h (ppm): 4.63 (Si-H, d); 5.85-5.78 (-CH=, m); 0.05 (-CH_3, m). ^{13}C NMR δ_c (ppm): 1.14 (-CH_3).

Fabrication of a poly(tert-butyl acrylate) (PtBA) film for initial modulus and refractive index measurement

After 0.5 mol% of 2, 2-dimethoxy-2-phenylacetophenone was completely dissolved in *t*BA, the solution was filtered with a 1.0 μm Teflon filter. The P*t*BA film was fabricated in the same way as the stress-whitening films were. The solution was also spin-coated on the hypotenuse surface of a high-index right-angle prism (N-SF11 glass, n=1.7778). The layer on the prism was UV-cured and dried in the same way as the P*t*BA film was.

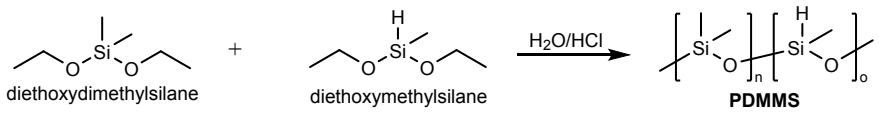
Fabrication of a PDMS film for initial modulus and refractive index measurements

First, 0.0030 g of platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution and 0.8078g of P06 were completely mixed together. 0.028 g of PDMMS was added to 0.229 g of the P06 containing the platinum catalyst and was completely mixed with the P06. The polymer mixture was casted on a glass plate and the high-index right-angle prism by Doctor-knife. The polymer layers were annealed at 70 ℃ under vacuum for 2 h, followed by removal of air bubbles from the layers at room temperature for 1 h under vacuum.

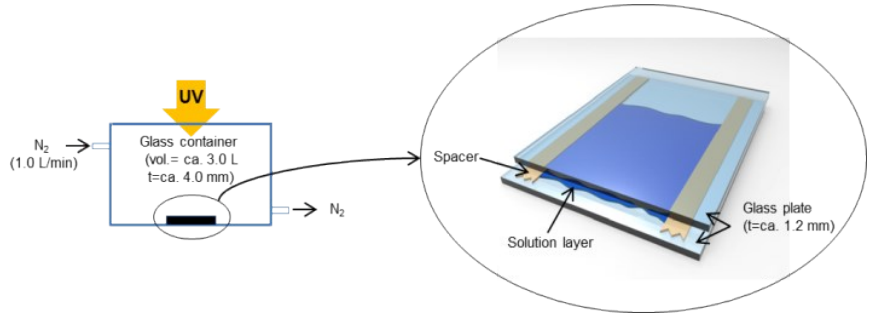
Calculation of solubility parameter (δ) of tBA and $\Delta\delta$ between tBA and PDMS by method Hoftyzer-Van Krevelen

The solution parameter components (δ_d, δ_p, δ_h) of a given material can be calculated from its group contributions using the following equations: $\delta d = \frac{\sum Fdi}{V}, \delta p = \frac{\sqrt{\sum F2pi}}{V}, \delta h = \sqrt{\frac{\sum Ehi}{V}}$, where δ_d, δ_p, and δ_h are a solubility parameter contributed by dispersion, polar, and hydrogen bonding components, respectively. F_{di} and F_{pi} are a molar attraction constant contributed by dispersion and polar components, respectively. E_{hi} is hydrogen bonding energy. V is a molar volume. The solubility parameter of a given material can be calculated using the following equation: $\delta = \sqrt{\delta d2 + \delta p2 + \delta h2}$. The solubility of a polymer in a solvent can be estimated using the following equation: $\Delta\delta = \sqrt{(\delta d,p - \delta d,s)2 + (\delta p,p - \delta p,s)2 + (\delta h,p - \delta h,s)2}$, where $\delta_{d,p}$, $\delta_{p,p}$, $\delta_{h,p}$ and $\delta_{d,s}$, $\delta_{p,s}$, $\delta_{h,s}$ are δ_d, δ_p, and δ_h of a polymer and solvent, respectively. $\Delta\delta$ means a 3D distance of solubility parameter between the polymer and solvent in a solubility sphere. The δ, δ_d, δ_p, and δ_h values for *t*BA ware calculated as shown in table S1. The values for PDMS and $\Delta\delta$ between PDMS and *t*BA were shown in table S2. The unit for δ are expressed as the square root of a cohesive energy density ($J^{1/2}\cdot cm^{-3/2}$) which is associated with intermolecular attractive interactions or as the square root of a pressure ($MPa^{1/2}$).

Schemes



Scheme S1 Synthesis of poly(dimethylsiloxane-*co*-methylsiloxane) (PDMMS).



Scheme S2 A schematic diagram of UV-cure equipment.

Figures

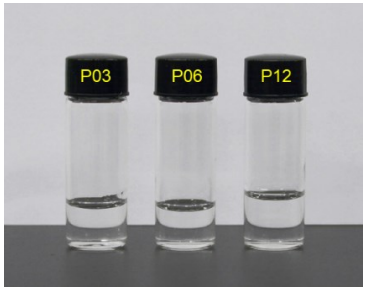


Fig. S1 A Photograph of PDMVS copolymers.

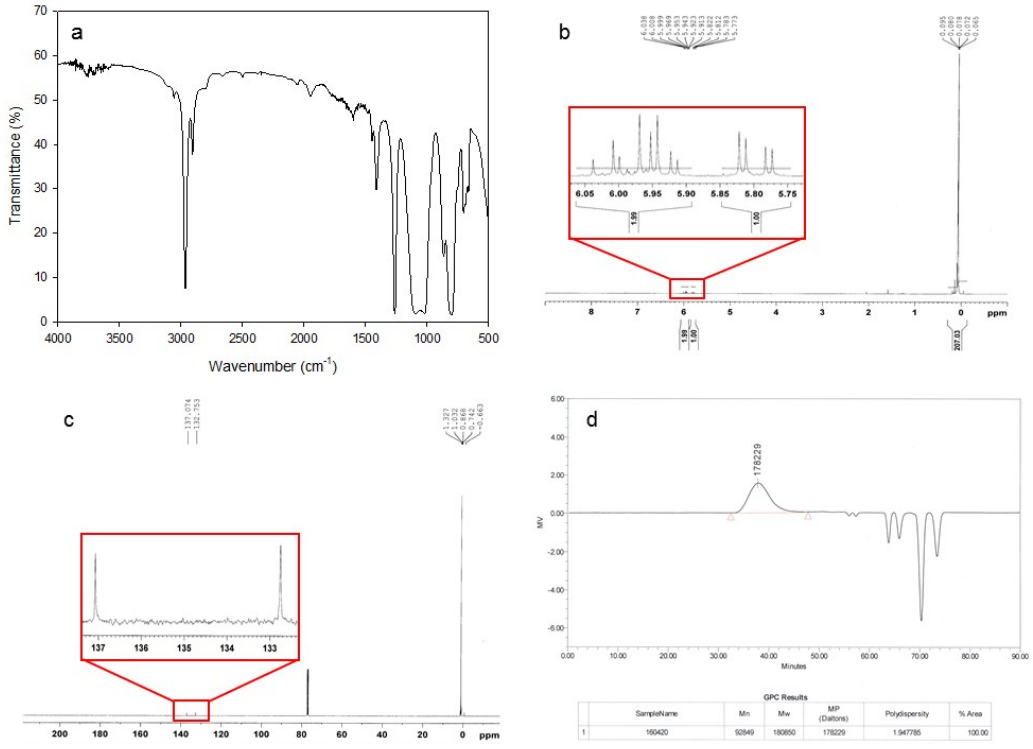


Fig. S2 IR (a), ^{1}H NMR (b), ^{13}C NMR (c) spectra, and GPC (d) results of poly(dimethylsiloxane-*co*-methylvinylsiloxane) (PDMVS) (97:3, mol%) (P03).

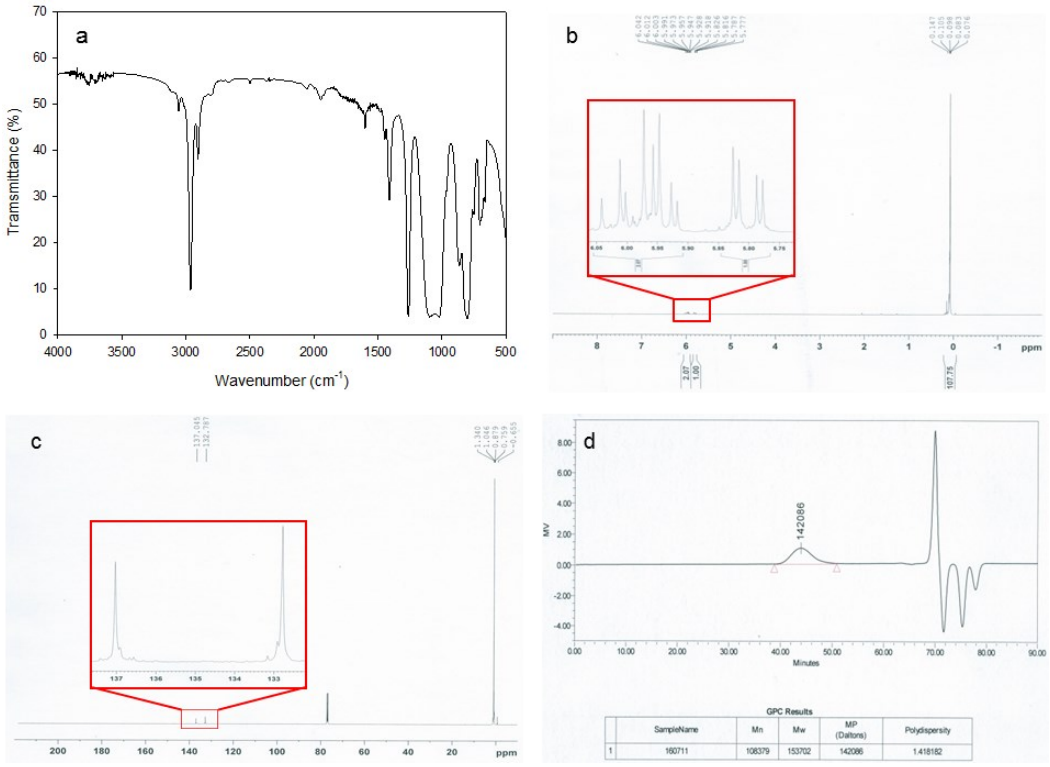


Fig. S3 IR (a), ^{1}H NMR (b), ^{13}C NMR (c) spectra, and GPC (d) results of poly(dimethylsiloxane-*co*-methylvinylsiloxane) (PDMVS) (94:6, mol%) (P06).

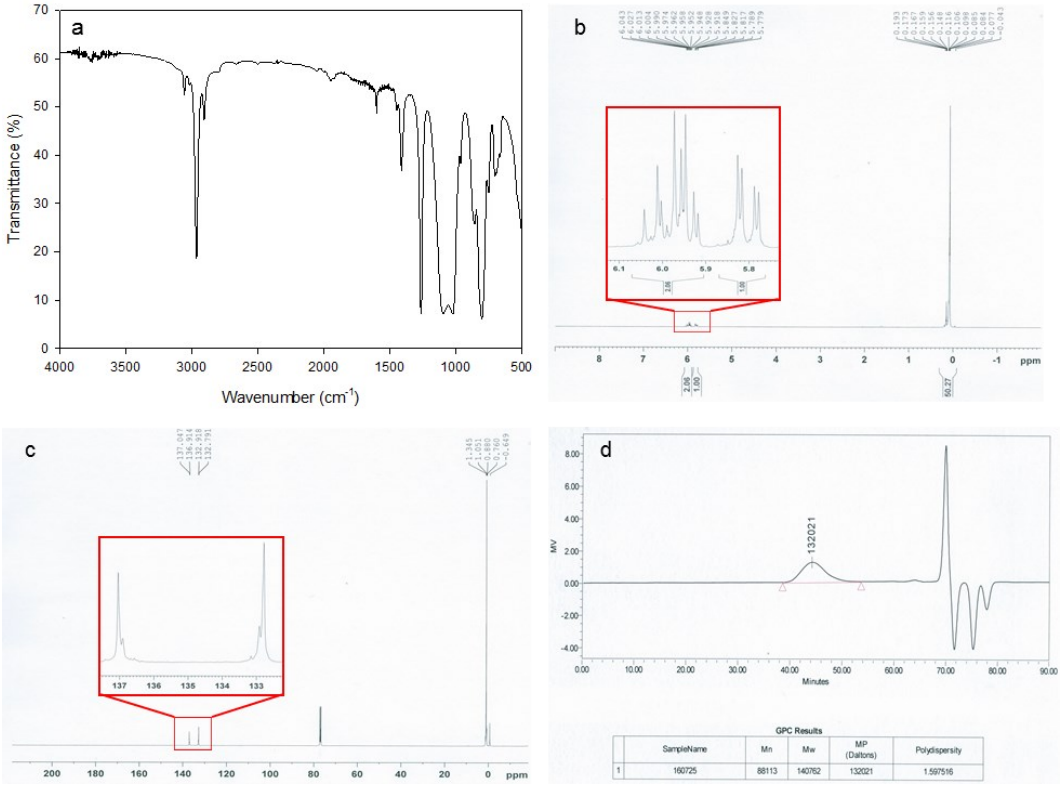


Fig. S4 IR (a), ^{1}H NMR (b), ^{13}C NMR (c) spectra, and GPC (d) results of poly(dimethylsiloxane-*co*-methylvinylsiloxane) (PDMVS) (88:12, mol%) (P12).

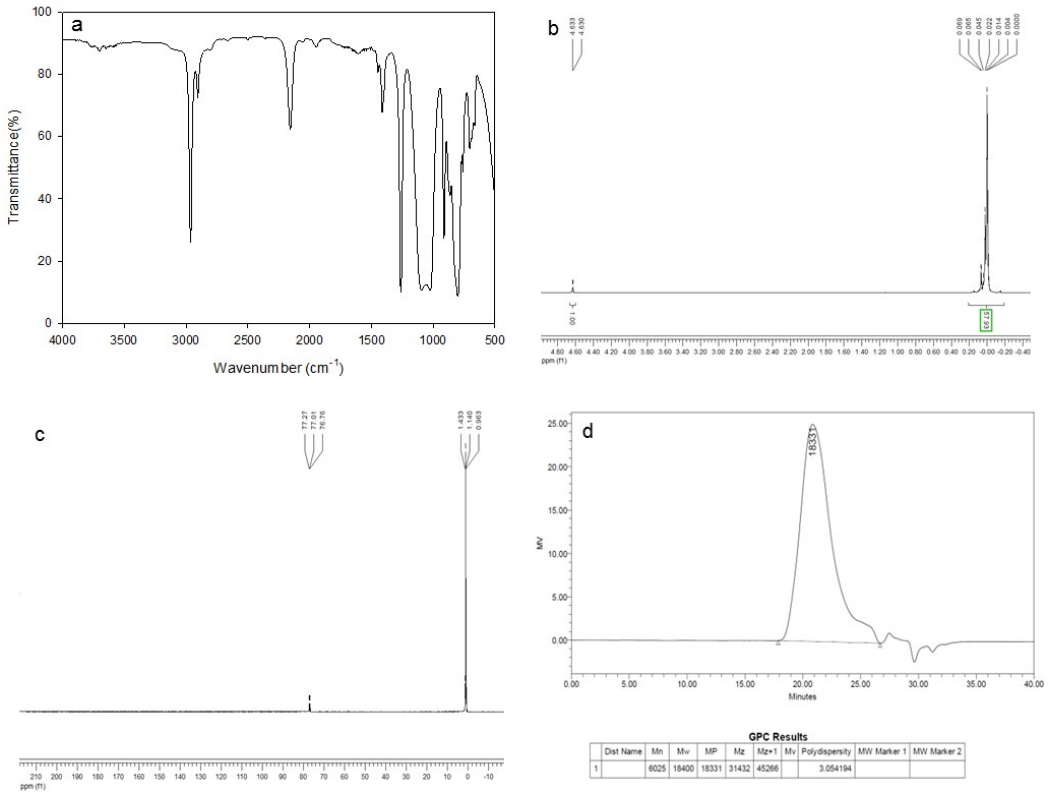


Fig. S5 IR (a), ^{1}H NMR (b), ^{13}C NMR (c) spectra, and GPC (d) results of poly(dimethylsiloxane-*co*-methylsiloxane) (PDMMS) (90:10, mol%).

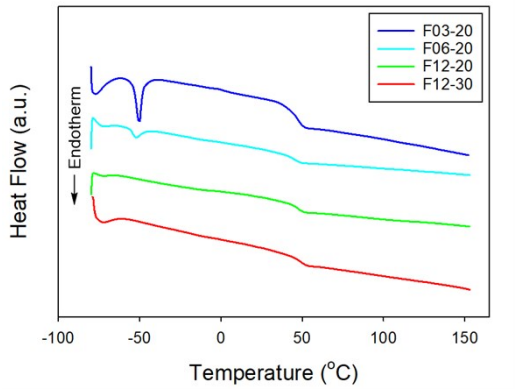


Fig. S6 DSC thermograms of the UV-cured films on the second heating.

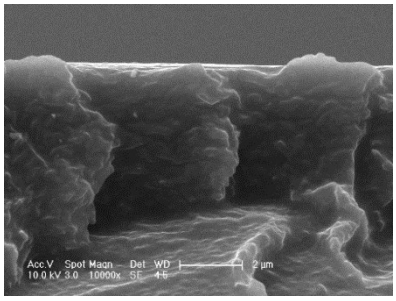


Fig. S7 A cross-sectional SEM image of the F06-20 film.

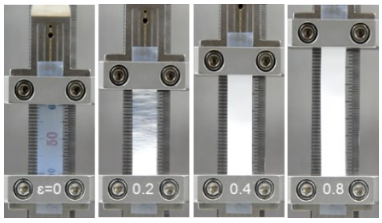


Fig. S8 Motion capture of the F06-20 film at each strain during drawing.

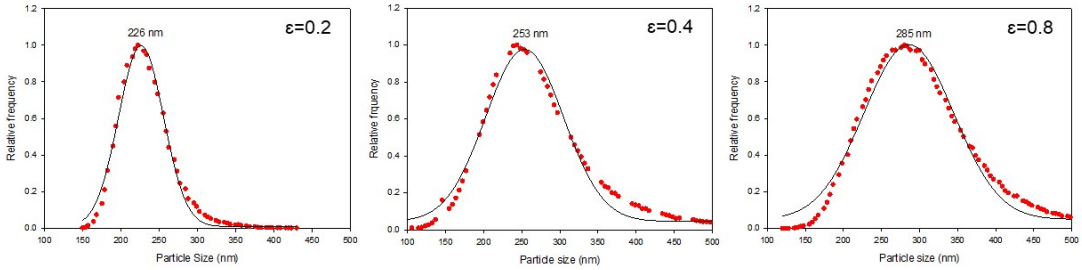


Fig. S9 A variation in size distribution of the P*t*BA nanoparticles packed into the F06-20 film with strain.

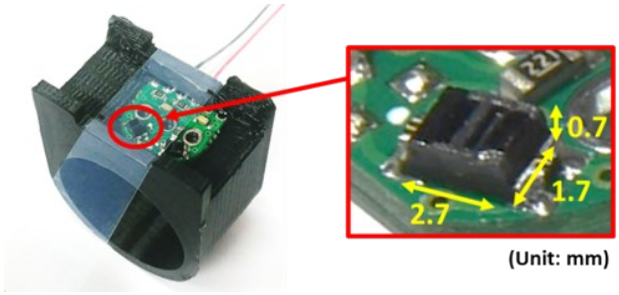


Fig. S10 A photograph of reflecting-type strain sensor established for human motion monitoring. The perforated frame putting on the index finger is used to facilitate finger movement during sensor performance test. The magnified view shows a detailed structure of optical transceiver module.

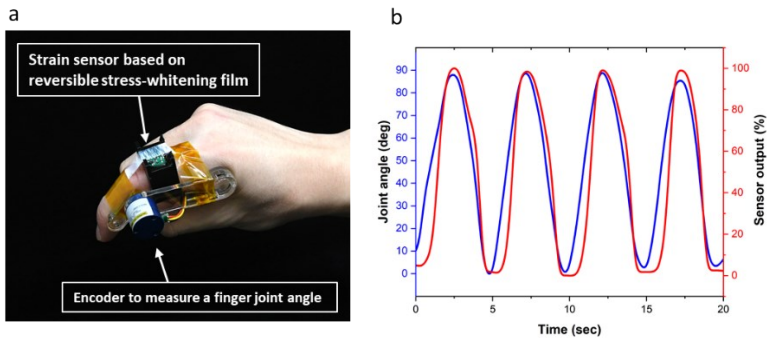


Fig. S11 A sensor performance test for real-time monitoring change in finger joint angle. An encoder measuring bending angle is mounted on the finger joint with a link system. Time-response of the reflecting-type strain sensor was simultaneously compared to the signal from the encoder.

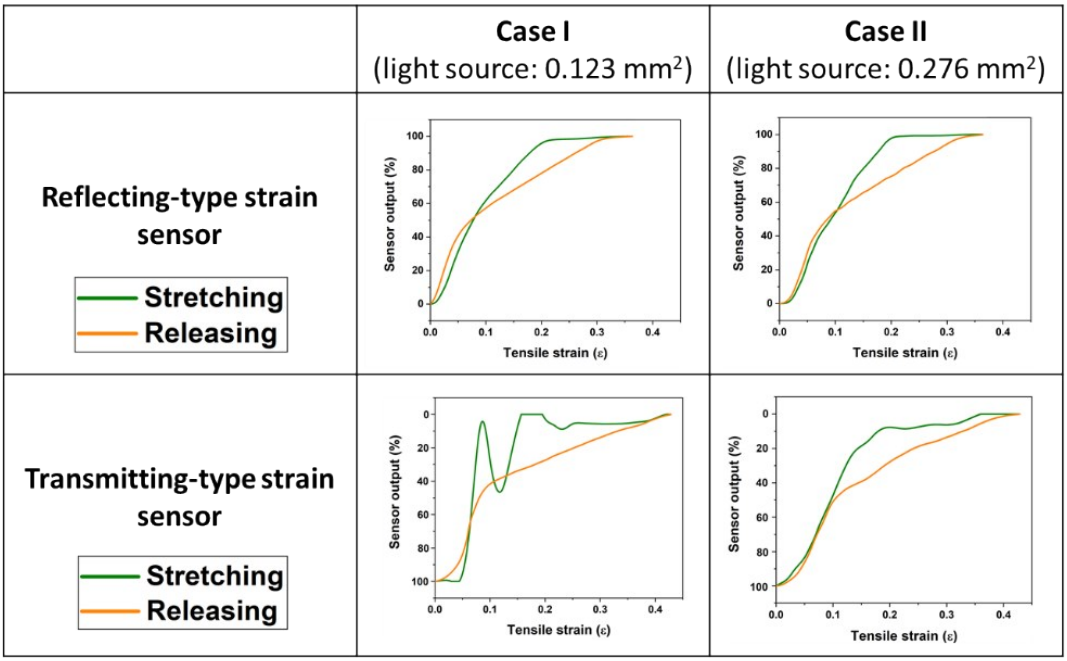
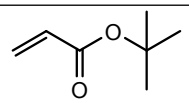


Fig. S12 The continuous sensor response of transmitting and reflecting-type strain sensor during an elongation-recovery cycle. In the case of the transmitting-type strain sensor with a small light source (case I), unstable sensor output is observed at the initial stage of elongation ($\varepsilon < 10\%$) due to an inconsistent position mismatch between a light illuminated spot and streaks irregularly generated at the elastomer film, while the reflecting-type strain sensor exhibits stable response regardless of size of a light source.

Tables

Table S1 Calculation of δ, δ_d, δ_p, and δ_h for *t*BA.

*t*BA		F_{di} ($J^{1/2}\cdot cm^{3/2}\cdot mol^{-1}$)	F_{pi} ($J^{1/2}\cdot cm^{3/2}\cdot mol^{-1}$)	E_{hi} ($J\cdot mol^{-1}$)
Chemical structure	Group contribution			
 M_w=128.17 d=0.875 g/mL at 25 °C[S1]	$-CH_3$ × 3	420 × 3	0	0
	-COO- × 1	390 × 1	490 × 1	7000 × 1
	$=CH_2$ × 1	400 × 1	0	0
	=CH- × 1	200 × 1	0	0
	 ×1	-70 × 1	0	0
Total		2180	490	7000

$$V_{tBA} = 128.17/0.875 = 146.48\ (cm^3 \cdot mol^{-1})$$

$$\delta d,tBA = \frac{2180}{146.48} = 14.9\ (MPa1/2)$$

$$\delta p,tBA = \frac{\sqrt{4902}}{146.48} = 3.35\ (MPa1/2)$$

$$\delta h,tBA = \sqrt{\frac{7000}{146.48}} = 6.91\ (MPa1/2)$$

$$\delta tBA = \sqrt{14.92 + 3.352 + 6.912} = 16.8\ (MPa1/2)$$

Table S2 $\bar{\Delta\delta}$ calculated from the three solubility components, δ_d, δ_p, and δ_h, of PDMS and *t*BA.

	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)	δ (MPa$^{1/2}$)	$\bar{\Delta\delta}$
PDMS	16.0	0.1	4.7	16.7	4.08
*t*BA	14.9	3.35	6.91	16.8	

$$\bar{\Delta\delta}\ (PDMS/tBA) = \sqrt{(16.0 - 14.9)2 + (0.1 - 3.35)2 + (4.7 - 6.91)2} = 4.08$$

Table S3 Composition of PDMVS solutions in *t*BA.

Name of polymer solution	P03 (g)	P06 (g)	P12 (g)	*t*BA[a)]	Acrylate/Vinyl groups (mole ratio)
S03-20	0.5176			2.0796	83.3
S06-20		0.7022		2.8468	43.0
S12-20			0.5208	2.0905	20.6
S12-30			0.9878	2.3090	12.0

[a)] *t*BA contains 0.5 mol% of a photoinitiator.

Table S4 UV lamp intensity applied on a solution layer.

Spectra	UV-V	UV-A	UV-B	UV-C
Intensity (mW/cm^2)	7.25	8.85	0.26	0.84

UV-V: 395~445 nm; UV-A: 320~390 nm; UV-B: 280~320 nm; UV-C: 250~260 nm (obtained from the manual of the radiometer).

Table S5 Mechanical properties of the stress-whitening films.[a)]

Film	Initial modulus (MPa)	Maximum stress (MPa)	Yield strain	Maximum strain
F03-20	15.67 (1.60)[b)]	3.49 (0.16)	0.103 (0.011)	1.02 (0.09)
F06-20	16.70 (2.28)	9.03 (0.53)	0.171 (0.003)	1.29 (0.14)
F12-20	34.24 (5.18)	12.95 (1.82)	0.173 (0.025)	1.06 (0.20)
F12-30	9.24 (0.68)	10.29 (0.27)	0.492 (0.063)	2.04 (0.15)

[a)]The properties were obtained from Fig. 2c. [b)]The values in parentheses mean standard deviation.

Movies

Movie S1 A video clip taken right after the reversible stress-whitening in a transparent PDMS film was discovered.

Movie S2 A video clip showing the F12-20 film drawn and recovered back by an Instron machine.

Movie S3 A video clip showing the application of strain sensor for human motion monitoring.

Reference

S1. Sigma-Aldrich, Online Product Catalog, https://www.sigmaaldrich.com/korea.html, (accessed November 2020).