

Algae-inspired, Sulfur-based Polymer with Infrared Transmission and Elastic Function

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ABSTRACT

This study prepared an elastic material with an infrared (IR)-transmitting property based on the structural features of algae oils. The bulk copolymerization of elemental sulfur and unsaturated hydrocarbons yields sulfur-based polymeric products, in a process termed inverse vulcanization. The inverse vulcanization of algae oils, such as squalene and botryococcene, forms highly cross-linked products owing to the multiple reaction sites along the long unsaturated backbone. Based on this structural feature, a combination of the algae oils and plant-based short-chain monoterpene compounds (D-limonene and β -myrcene) was investigated to provide a suitable cross-linking density for achieving an elastic function. Inverse vulcanization of squalene and β -myrcene produced an elastic material with an IR-transmitting property. The developed material served as a varifocal lens in the IR region that responds to external elongation forces. From the viewpoint of sustainability, it is meaningful that the material was produced from sustainable feedstocks (algae and plant oils) and a surplus feedstock (sulfur).

1. INTRODUCTION

The bulk free-radical copolymerization of elemental sulfur and unsaturated hydrocarbons produces

sulfur-based polymeric products.^{1,2} This method is termed inverse vulcanization and it enables the effective utilization of a surplus feedstock, sulfur, which originates from desulfurization in petroleum refinery processes. Sulfur-rich products serve as cathode active materials in Li-S batteries,^{1,3,4} self-healing materials^{5,6}, metal scavengers^{7,8}, oil adsorbents⁹ and adhesives^{10,11}, slow-release fertilizers¹², disinfection materials¹³, and recyclable composites¹⁴ by taking advantage of reversible S-S bonds, coordination ability, and simple preparation processes. Optical applications in the infrared (IR) region are also expected from sulfur-rich materials^{5,15-21} because some of them exhibit light transmission in the IR region superior to that of common organic materials. One of the advantages of these materials is their high processability due to thermoplasticity, which is not achieved in conventional inorganic IR materials such as Ge, Si, and ZnSe.^{1,22} Although the demand for industrial applications of IR cameras, such as equipment monitoring in automated factories and night vision for security, is rapidly expanding, conventional IR-transmission lenses are still expensive. Sulfur-based materials are expected to be utilized as new materials with low cost and high processability. In addition to the properties of IR transmission and thermoplasticity, we recently intended to introduce one more interesting feature, elasticity, to sulfur-based polymers. Because the elasticity of the materials allows the reversible deformation of their bulk shape, the radius of the lens curvature made from such materials can be tuned by stretching for focal length adjustment.^{23,24} Considering a basic principle in polymer chemistry, the cross-linking density

should be vital for the development of elastic materials.²⁵ For tuning the cross-linking density in inverse vulcanization, combining unsaturated hydrocarbons²⁶⁻³⁰ is a reasonable strategy. Hassel and coworkers have reported that physical properties such as glass transition temperature (T_g), tensile, and flexural strength of the terpolymers can be tuned by changing the composition of unsaturated hydrocarbons.²⁹ An appropriate combination of long and short unsaturated hydrocarbons is expected to yield the desired cross-linking structure for achieving objective elasticity because a long unsaturated hydrocarbon bearing a large number of double bonds has a higher chance of forming cross-linking points than a short chain.²⁶ Although the preparation of long unsaturated hydrocarbons requires multiple synthetic steps,^{31,32} certain algae produce algae oils composed of long unsaturated hydrocarbons, such as squalene and botryococcene, in a selective and efficient manner.³³⁻³⁵ The structural features and efficient production of algae oil are suitable for developing elastic IR-transmitting materials via inverse vulcanization. In this research, plant-based monoterpene compounds were selected as short-chain comonomers in order to achieve material production from sustainable feedstocks. Herein, we report the development of elastic IR-transmitting materials designed from the structural features of algae and plant oil and discuss its interesting and useful application as a variable-focus lens that can work in the IR region.

2. EXPERIMENTAL SECTION

2.1. Materials

Elemental sulfur was purchased from Kanto Chemical Co., Inc. Squalene, D-limonene, and β -myrcene were purchased from Tokyo Chemical Industry Co., LTD. Botryococcene was provided from ABES in University of Tsukuba. Kapton (Polyimide) film was purchased from Japan Manufacturer Trade, Inc. Mold making silicone (KE-1606) was provided from Shin-Etsu Chemical Co., Inc.

2.2. Method

Differential scanning calorimetry (DSC) was conducted in aluminum pans using a Shimadzu DSC-60 Plus. The condition of DSC was under 50 ml min⁻¹ N₂ flow, with heating and cooling rates of 10 °C min⁻¹. Fourier Transform Infrared (FT-IR) spectrum was recorded on JASCO FT-IR 4600 spectrometer. For FT-IR spectroscopy, sample films with thickness of 0.22 mm were prepared by a hot press machine at 120 °C for 1 min. Pencil hardness tests were conducted on JIS 5600-5-4 (ISO/DIS 15184). Tensile stress–strain curves of the sample films were collected by AND Force Tester MCT-2150 according to JIS K 6251 (ISO 37). The thickness and width of the test films were typically 5 and 10 mm, respectively. The initial gauge length was set to 30 mm. IR laser beam

($\lambda = 5.1 \mu\text{m}$) was generated from CW Quantum Cascade Laser (Pranalytica, Inc., Model: 1101-52-CW-50-TT). A transmitted light pattern through the elastic cylindrical lens was detected by a thermal camera (As One, TIM-03).

2.3. Inverse vulcanization reaction of S₈, Squalene, and β -Myrcene (Table 2, Entry 4)

Elemental sulfur (0.50 g, 16 mmol), squalene (0.30 g, 0.73 mmol), β -myrcene (0.20 g, 1.5 mmol), and a magnetic stirrer bar were placed in a 10 mL open glass vial. The mixture was stirred (550 rpm) at 185 °C for 30 minutes by using aluminum heating blocks. The product was poured on a Kapton film and collected after cooling to room temperature.

2.4. Two-step inverse vulcanization reaction for preparation of a test piece

Elemental sulfur (0.50 g, 16 mmol), squalene (0.30 g, 0.73 mmol), β -myrcene (0.20 g, 1.5 mmol), and a magnetic stirrer bar were placed in a 10 mL open glass vial. The mixture was stirred (550 rpm) at 185 °C for 4 minutes by using aluminum heating blocks. The prepolymer was poured into a silicon mold. The prepolymer in the mold was heated in an oven at 120 °C for 4 hours. The product was collected after cooling to room temperature.

2.5. Verification of basic performance as a variable focus IR lens

The experimental setup was shown in Figure S5 in supporting information. A cylindrical lens of

Polymer 2 (Table 3) was prepared with a concave silicone resin mold, that was replicated with a glass cylindrical lens with 10 mm-radius of the curvature as a master. An arrow-shaped light pattern was generated by illuminating an arrow-shaped optical mask (a stencil plate) by a collimated IR laser beam ($\lambda = 5.1 \mu\text{m}$) with 8 mm-diameter. The arrow-shaped light pattern was monitored by a thermal camera through the cylindrical lens while the lens was elongated to 1.33-times length and recovered to the initial length. The video was uploaded as a supporting information file and the snapshots were shown in Figure 5.

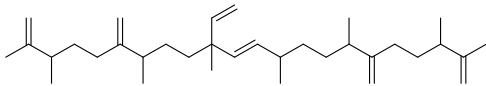
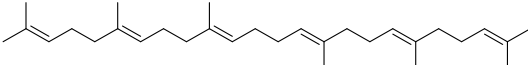
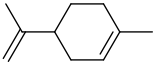
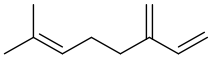
3. RESULTS AND DISCUSSION

3.1. Investigation of the appropriate composition for a new elastic IR transmitting material

Inverse vulcanization reactions were conducted to investigate the relationship between the structure of oils and properties of the products (Table 1). Botryococcene³⁴ and squalene³⁵ were selected as long-chain unsaturated hydrocarbons bearing 6 double bonds. D-limonene⁷ and β -myrcene^{8,36} were plant-based short-chain monoterpene compounds bearing two and three double bonds, respectively. Although inverse vulcanization reactions of these oils were reported before, the reactions with them were re-examined under identical reaction conditions to compare reactivity of the oils and properties of the products. While the reactions of botryococcene and squalene

yielded hard resin-like products (Entries 1 and 2), the reactions of D-limonene and β -myrcene yielded oily products (Entries 3 and 4). These results suggest that the reactions of substrates bearing a large number of double bonds yielded highly cross-linked products. Hardness tests show that the botryococcene-based product is softer than the squalene-based products (Entries 1 and 2). In our previous work, the inverse vulcanization reactions of botryococcene formed products with loop structures via intramolecular cyclization, which probably decreased the cross-linking density and softened the product. This hypothesis is supported by the fact that the botryococcene-based product has a higher solubility than the squalene-based products.

Table 1. Solubility and hardness of the inverse vulcanization products ^[a]

Entry	Oil	Solubility ^[b]	Pencil hardness test ^[c]
1	 <p>Botryococcene</p>	Soluble	F
2	 <p>Squalene</p>	Partly soluble	3H
3	 <p>D-Limonene</p>	Soluble	Soft
4	 <p>β-Myrcene</p>	Soluble	Soft

^[a] Reaction conditions: 185 °C, 40 min, S₈ : oil = 5 : 5 (weight ratio).

^[b] Solubility tests were conducted at 10 mg/mL in CHCl₃ at room temperature.

^[c] JIS 5600-5-4.

The combination of algae oils and monoterpene compounds was examined to control the cross-linking structure (Table 2). The reaction with botryococcene and D-limonene yielded a flexible product that can be fabricated in a free-standing film (Entry 1). The color of the film turned yellow from reddish-brown over time. This phenomenon is called blooming, and suggests the presence of unreacted elemental sulfur in the product. Chalker and co-workers reported that D-limonene turned to *p*-cymene via dehydrogenation during inverse vulcanization.⁷ Since *p*-cymene is inactive for inverse vulcanization, this side reaction results in a shortage of the reactive double bonds required

for the incorporation of sulfur atoms in the polymeric network. The reaction with β -myrcene as a comonomer yielded a soft product, causing no blooming (Entry 2). This result shows that β -myrcene is an appropriate choice as a comonomer. The product in Entry 2 shows a low T_g value and high solubility in CHCl_3 , suggesting a limited cross-linking structure. The reaction of squalene with β -myrcene afforded a flexible material with a relatively high T_g and low solubility (Entry 4), which is reminiscent of higher cross-linking density, in comparison with the products in Entries 1 and 2. As squalene was found to be more suitable than botryococcene for forming cross-linking structures, the effects of the weight ratio of sulfur, squalene, and β -myrcene were investigated in terms of T_g and solubility (Table 2, Entries 3-5). The increased ratio of squalene tends to increase the T_g and lower the solubility of the products. These results show that products with higher squalene content have a larger number of cross-linking points. ^1H NMR spectra of the products in Entry 3-5 show small signals in the olefinic region (Figure S1), which means that most of the olefinic groups are reacted with sulfur. Remaining small signal at 5.1 ppm is assigned to the protons of the olefinic group in squalene. In terms of viscoelastic characteristics, the product in Entry 2 is only plastically deformed by an external force. In contrast, a preliminary trial revealed that the product in Entry 4 exhibited an elastic function, indicating that the combination of sulfur, squalene, and β -myrcene is a promising candidate.

Table 2. Results of inverse vulcanization of blended oils ^[a]

Entry	Raw material (weight ratio)	T_g (°C)	Solubility ^[b]
1	S ₈ : Botryococcene : D-Limonene (5:3:2)	5.0	Soluble
2	S ₈ : Botryococcene : β-Myrcene (5:3:2)	3.3	Soluble
3 ^[c]	S ₈ : Squalene : β-Myrcene (5:4:1)	20.4	Partly soluble
4 ^[c]	S ₈ : Squalene : β-Myrcene (5:3:2)	11.6	Partly soluble
5 ^[c]	S ₈ : Squalene : β-Myrcene (5:2:3)	7.9	Soluble

^[a] Reaction conditions: 185 °C, 40 min

^[b] Solubility tests were conducted at 10 mg/mL in CHCl₃ at room temperature.

^[c] 30 min.

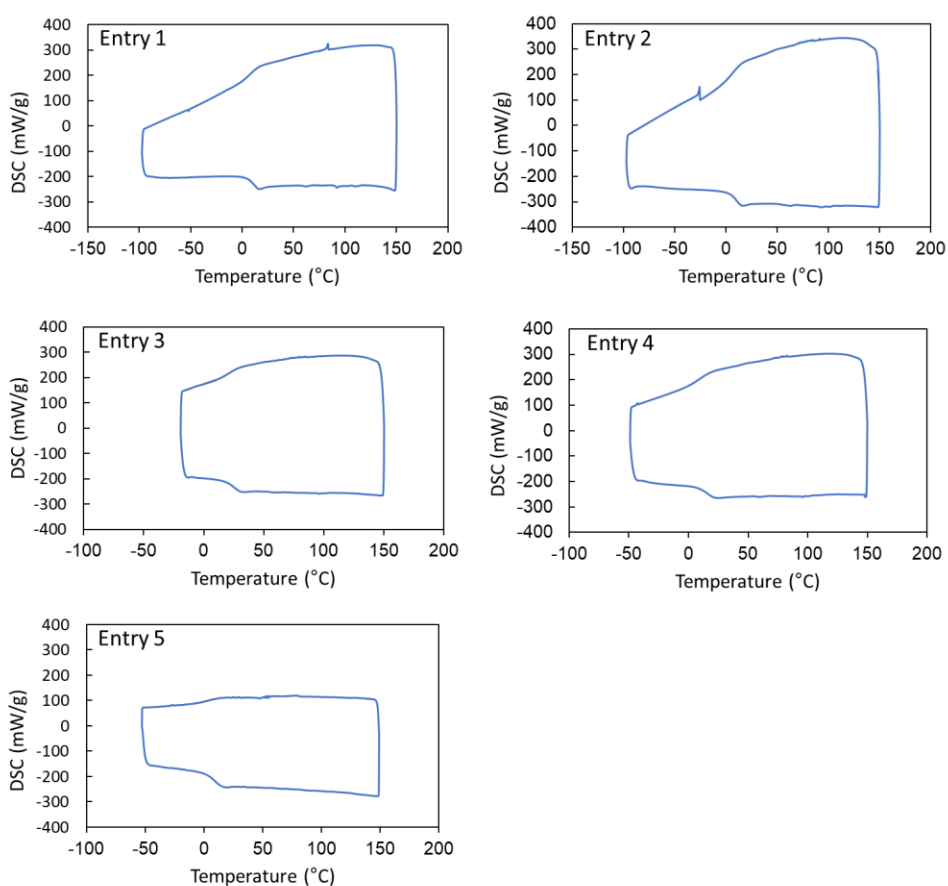


Figure 1. DSC thermograms of the samples in Table 2.

The elastic functions of the products in Entries 3, 4, and 5 were evaluated by 20% elongation and recovery tests (Figure 2, Figure S2). The sample with the highest squalene content (Entry 3) was broken at the first elongation. The sample in Entry 4 recovered to its initial length after three instances of elongation. In contrast, the sample in Entry 5 showed a partial plastic deformation behavior where it did not recover to its initial length as the number of trials increased. These results show that the sample in Entry 4 (S_8 : squalene : β -myrcene = 5:3:2) possesses a suitable cross-linking structure that imparts the desired elastic function. The subsequent cycle test showed that the sample in Entry 4 was able to recover to its initial length in at least 10-cycle trials (Figure S3).

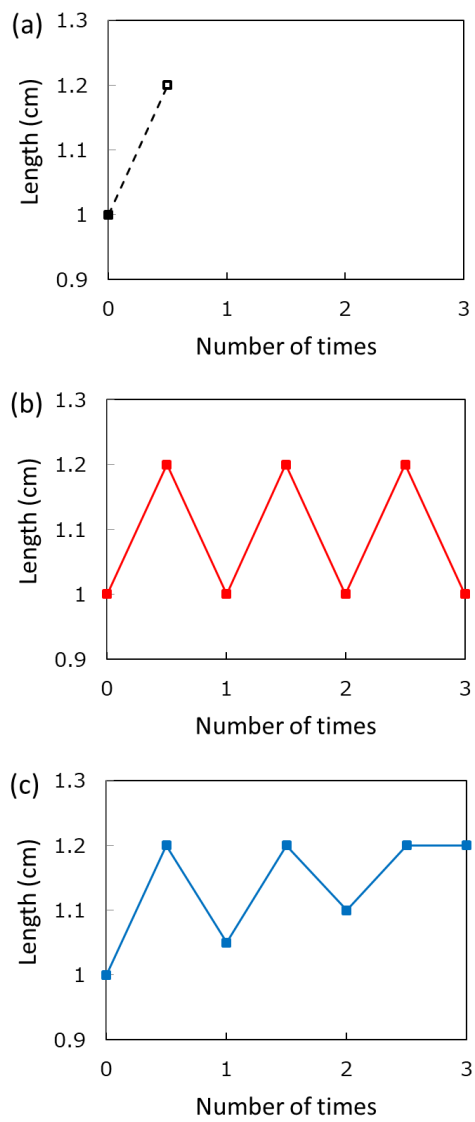


Figure 2. Evaluation of elastic functions of the samples of (a) Entry 3, (b) Entry 4, and (c) Entry 5 in Table 2. Sample size: 5 mm thick and 10 mm wide.

3.2. Physicochemical examination of the elastic function

The combination of sulfur, squalene, and β -myrcene resulted in the formation of the elastic material through the inverse vulcanization reaction. For detailed investigation, viscoelastic

measurements were conducted on the samples with varying compositions. Although viscoelastic measurements require specific dumbbell-shaped test pieces, the above-mentioned samples in Table 2 have limited processability. Therefore, a two-step protocol was utilized for preparing intended shapes as reported by Puyn and Hasell.^{1,30} First, a prepolymer with fluidity was obtained through a reaction for 4 min at 185 °C. Then, the prepolymer was poured into a silicon mold and heated for 4 hours at 120 °C. The samples prepared through this protocol (Polymer 1, 2, and 3) showed similar T_g and solubility (Table 3) to the corresponding samples prepared using the one-step protocol (Table 2). This observation shows that these protocols give almost identical materials. Figure 3 shows stress-strain curves of Polymer 1, 2, and 3 and the obtained Young's modulus values are listed in Table 3. Polymer 1, possessing the highest squalene content, has the largest Young's modulus value (9.5 MPa) and the smallest value of elongation at break, indicating the highest cross-linking structure. The reduction of the squalene content decreases the Young's modulus values, and increases elongation at break (Table 3, Figure 3). The results of viscoelastic measurements support our molecular design that a long unsaturated hydrocarbon (squalene) provides more cross-linking points. The stress-strain curve of Polymer 2 exhibits a linear response in the range of 20% elongation (Figure 3), indicative of elastic properties, which was observed in the elongation and recovery test (Figure 2b). In addition to length, the initial shape of an object can be recovered after releasing the external forces (See Supporting Information). The detailed

physicochemical investigation also reveals that S_8 : squalene : β -myrcene = 5:3:2 is the suitable ratio for achieving elastic materials.

Table 3. Physicochemical properties of Polymer 1-3. ^[a]

	S_8 : Squalene : β -Myrcene (Weight ratio)	T_g (°C)	Solubility (CHCl ₃) ^[b]	Young modulus (MPa)
Polymer 1	5:4:1	15.0	Partly soluble	9.5
Polymer 2	5:3:2	10.4	Partly soluble	0.67
Polymer 3	5:2:3	8.8	Soluble	0.13

^[a] Reaction conditions: 185 °C, 4 min, 120 °C, 4 hours.

^[b] Solubility tests were conducted at 10 mg/mL at room temperature.

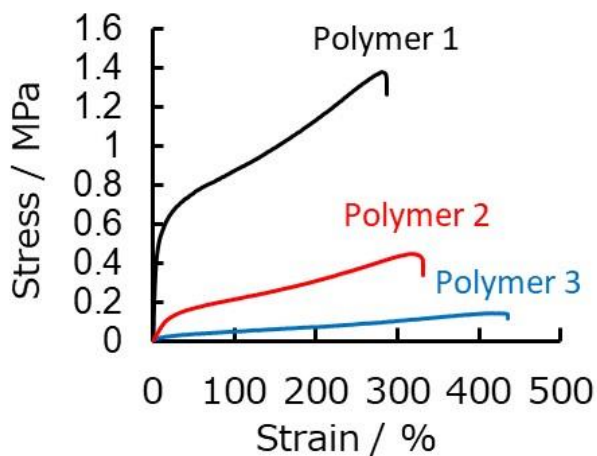


Figure 3. Stress-strain curve of Polymer 1, 2, and 3 (JIS K 6251).

3.3 Verification of basic performance as a variable focus IR lens

Further investigation into its capability as an IR-transmission material with elasticity was performed on polymer 2. As shown in Figure 4, it exhibits two transparent regions that are separated by a strong absorption band at approximately 3100-2700 cm^{-1} between the short- and mid-wavelength IR regions. They are 4000-3350 cm^{-1} (2.60-2.78 μm) and 2200-1750 cm^{-1} (4.76-5.56 μm), if we define the wave numbers at which the absorption coefficient is less than 3 cm^{-1} as the characteristic value. This numerical value corresponds to a superior transparency wherein 10% transmission of incident IR light can be achieved even if a lens element having a thickness of 3.3 mm (that is, the maximum value of the lens employed in this experiment) is considered. In the most transparent region at 1965 cm^{-1} , the absorption coefficient is less than 1 cm^{-1} . To confirm the variable-focus characteristics using a simple deformation experiment, a cylindrical lens with a maximum thickness of 3.3 mm was prepared from Polymer 2 (Figure S4). The prepolymer was poured into a concave silicone resin mold, which was replicated from a glass cylindrical lens with a 10 mm radius of curvature as a master. The curing reaction of the prepolymer in the mold resulted in the formation of a cylindrical lens bearing the same curvature as the original glass lens. The estimated focusing length of the obtained lens was approximately 15.4 mm. An arrow-shaped pattern of the IR laser beam ($\lambda = 5.1 \mu\text{m}$) was used for confirming the variable-focus function of

the cylindrical lens. An arrow-shaped optical mask (a stencil plate) was illuminated by a collimated laser beam with 8 mm-diameter. The generated arrow-shaped light pattern was monitored using a thermal camera through the cylindrical lens (Figure S5). Figure 5 shows the observation results of the shape change of the arrow pattern due to the deformation of the cylindrical lens. Figure 5a shows an extended arrow shape flipped in a horizontal direction, which means that the laser light was detected after the focal points of the cylindrical lens (Figure S6). According to the lens elongation, it was observed that the arrow shrank in the horizontal direction (Figure 5a-c). Figure 5c shows the image obtained when the lens was stretched to 1.33 times its length and the width was reduced to approximately half. From this result, it can be estimated that the focal length of the lens is extended to approximately 23.7 mm (Figure S7). That is, when considering the focal length in the initial state as a reference, approximately 54% of the focus variability was experimentally confirmed. This value is considered to be sufficiently large from a practical viewpoint. After removing the extension force, the lens recovered to its original shape, and almost the same image as the initial one was observed (Figure 5d and e). From this demonstration, it can be said that basic performance as a variable-focus IR lens was exhibited by Polymer 2.

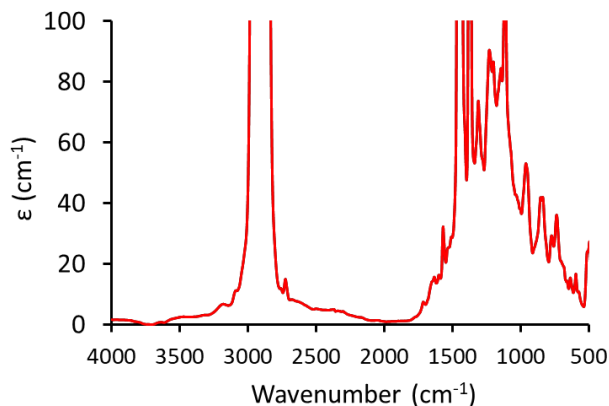


Figure 4. FT-IR spectrum of Polymer 2.

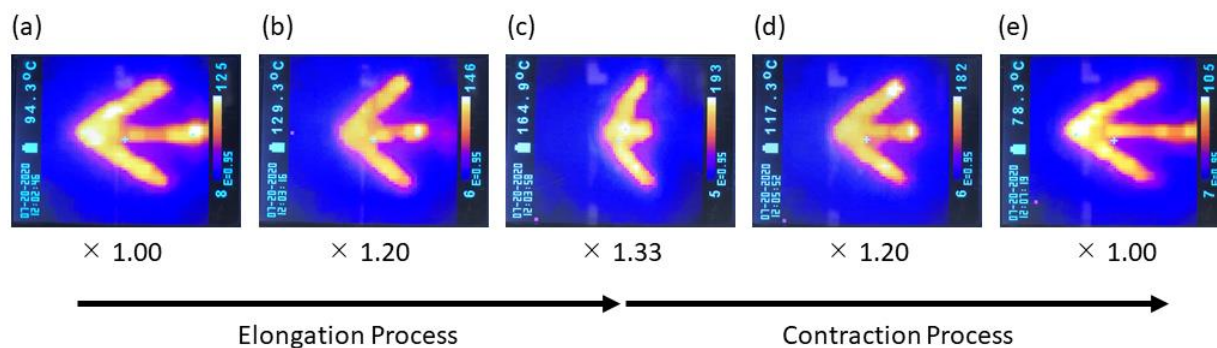


Figure 5. Snapshots of transmitted arrow patterns of IR light that change during stretching and shrinking of the sample; at (a) the initial length, elongated to (b) 1.2 times, (c) 1.33 times, and contracted to (d) 1.2 times and to (e) the initial length.

4. CONCLUSION

Elastic IR-transmitting materials was successfully developed after considering the structural features of algae oil. Algae oil provided cross-linking points in sulfur-based materials formed

through inverse vulcanization owing to multiple reaction sites in its long unsaturated backbone. An appropriate combination of algae oil and short-chain monoterpene compounds provides a suitable cross-linking density for achieving the desired elastic function, which enables reversible elongation and recovery. In addition, as an application example that makes use of both the elasticity and IR-transmission characteristics of the material, variable-focus characteristics were demonstrated for IR light using a simple cylindrical lens made of the developed material. This demonstration shows its potential application as a unique material in IR optics. In addition, it is noteworthy that the raw materials of the developed polymer possess low environmental impact. This is considered as a significant contribution to meeting the global needs of realizing a sustainable society.

ASSOCIATE CONTENT

Supporting Information. Demonstration video of an elongation/recovery property and a variable focus property of the IR lens, DSC curves, photograph of the samples, details of the experimental setups. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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