Supporting Information

A Non-Conjugated Photothermal Polymer Complex Absorbing Light in Visible and Infrared Windows

Ruiting Li,[+] Zhen Wang,[+] Xinglei Tao, Shanzhi Lyu, Jichen Jia, Xiao-Qi Xu and Yapei Wang*

Department of Chemistry, Renmin University of China, Beijing 100872, China

[+] These authors contribute equally to this article.

EXPERIMENTAL SECTION

Materials:

Polystyrene-b-polybutadiene-b-polystyrene (SBS, D1101J) and poly(styrene-ethylene/butylene-styrene) (SEBS) were obtained from Kraton. Iodine (I_2) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), N-iodosuccinimide (NIS), N-Chlorosuccinimide (NCS), N-Bromosuccinimide (NBS), iodosobenzene diacetate ($PhI(OAc)_2$), tetrahydrofuran (THF), acetonitrile (MeCN), dimethylsulfoxide (DMSO), methanol (MeOH), n-hexane, dichloromethane (DCM), toluene, dioxane, cyclohexane and chloroform (TCM) were purchased from Beijing Chemical Works.

Characterization methods:

Optical images were captured by a digital camera (Olympus, E-PM1). Viscometer (Lovis 2000 M/ME, Anton Paar Shanghai Trading Co., Ltd.) was used to collect the viscosities of these solutions. UV-Vis-NIR spectrophotometer (SHIMADZU-UV3600) was used to acquire the absorption spectra of SBS with different degree of iodine doping. The reflection spectra were recorded on a UV-Vis-NIR spectrophotometer (SHIMADZU-UV3600PLUS). Fourier transform infrared (FTIR) spectra were obtained on a Bruker IFS66v FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained by a Bruker 400 MHz spectrometer in $CDCl_3$. Electron paramagnetic resonance (Bruker ELEXSYS E580 Spectrometer) was used to determine the existence of free radicals in the iodine doped SBS in toluene in the liquid nitrogen environment. NIR-light irradiation with different light power densities were recorded by an infrared camera (Fluke Tix 660), and were analyzed by a software (Smartview). Solar simulator (product model: SOLARBEAM-02-3A, CROWNTECH, INC) was used as light source to provide light energy. Fresnel lens was utilized to improve the light powers.

Fabrication of SBS-I_2 solutions and organogels:

Solution casting technology was used in preparing the organogels. Firstly, SBS was dissolved in chloroform with a concentration of 50 mg/mL. Then, iodine was added with constant stirring. As the solution get more viscous, the organogel was gradually formed. Before it is immobile, it can be easily processed by virtue of liquid fluidity to make any shapes.

Calculation of the double bonds in the SBS:

As shown in the ^{1}H-NMR spectrum (Figure S4), the integral of all protons on the benzene rings was set as 1.00 which corresponds to the peaks from 6.25 ppm to 7.25 ppm. All peaks at other chemical shifts were integrated according to this setup. Signal j was regarded as from 4.85 ppm to 5.05 ppm. The integral of signal i was evaluated from that of the signal j because they are on the same double bonds, rather than to integrate it. The entire integral of protons at i and e on double bond was obtained from 5.10 ppm to 5.70 ppm. The corresponding integral of e peak was calculated by subtracting the integral of signals i from the entire integral of protons at i and e on double bond. As shown in Figure S3, the integrals of signal j, i, and e are 0.23, 0.115, and 1.525.

So,

$$\frac{5(m+n)}{1} = \frac{2p}{1.525} = \frac{3q}{0.345}$$

The molecular weight M of SBS can be represented by

$$M = 104.15(m+n) + 54.09(p+q)$$

According to the equations above, it can be calculated that the molar ratio between SBS of 150 mg to iodine of 500 mg is 1:1.

Photothermal conversion test of organogel:

The photothermal conversion performance of the iodine doped SBS samples was tested under 808 nm laser (HTOE, Beijing, China) and 1064 nm laser ((FS1064-5000-1; Wavicle Laser Co.) with different light power densities (0.1, 0.3, 0.5, 0.7, 0.9 and 1.1 W/cm^2, respectively). Each NIR illumination was lasted for 3 min followed by cooling at room temperature for 3 min. The whole process was repeated for three times to evaluate the thermostability. Their surface temperature changes were recorded by an infrared camera.

Calculation of photothermal conversion efficiency:

The photothermal conversion efficiency (η) can be calculated according to eq (1):

$$\eta = \frac{Q}{P}$$

(1)

Where Q is the heat per unit time produced by light irradiation and P is the light power. The key factor in the equation is Q. At a specific point in a typical heating process, the following equation should be satisfied:

$$mCp(T)\frac{dT}{dt} = Q - hA(T - T_0)$$

(2)

Where h is the heat transfer coefficient, and A is the surface area of the system. T is the temperature of the slice at a certain time t and T_0 is the ambient temperature. C_p is the specific heat of the slice. In this system, the C_p differs from the temperature changes, which could be determined by a method of sapphire with DSC instrument. $f(T)$ is defined as dt/dT, which can be figured out through differential operation of the inverse function of temperature-rising curve. $g(T)$ is defined by eq. (3):

$$g(T) = \frac{Cp(T)}{f(T)} = -\frac{hA}{m}T + \frac{Q + hAT_0}{m}$$

(3)

As Cp and $f(T)$ are given at a certain temperature T, $g(T)$ against temperature T can be fitted as a linear equation. According to this linear equation, the slope and intercept are $-\frac{hA}{m}$ and $\frac{Q + hAT_0}{m}$ respectively. The Q could be thereby calculated as below:

$$Q = m(b - aT_0)$$

(4)

The photothermal conversion efficiency as a function of Q can be thus calculated. The photothermal conversion efficiency is estimated as 46.8%.

Coating preparation on the pot:

The outdoor photothermal conversion measurement was carried out with a pot coated with

an SBS-I$_2$ layer at the bottom. A more detailed experimental process to fabricate the SBS-I$_2$ layer is as follows: 40 mL of SBS-I$_2$ chloroform solution was stirred at room temperature for 2 h, allowing the double bonds and iodine to react evenly, until the solution became a gel-like state. Then, the gelatinous solution was uniformly coated on the bottom of the pot with a brush like painting. The pot was purchased from the SUPOR with a diameter of 24 cm which could hold 2 L water inside. After the solvent was dried in the fume hood for several hours, the SBS-I$_2$ layer strongly adhered to the bottom of the pot. The bottom of the pot was further treated at 250∘C for 2 hours for its use in the photothermal conversion measurement.
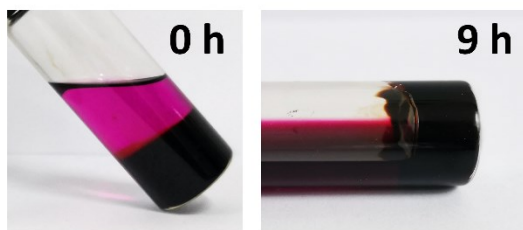
Figure S1. Optical images of the gel-like solids dissolved in chloroform for 0 h and 9 h.
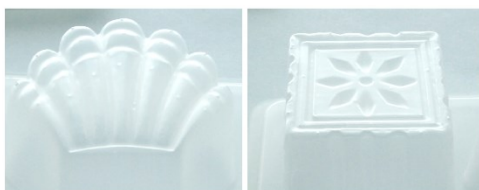
Figure S2. Optical images of the molds used in the casting process.

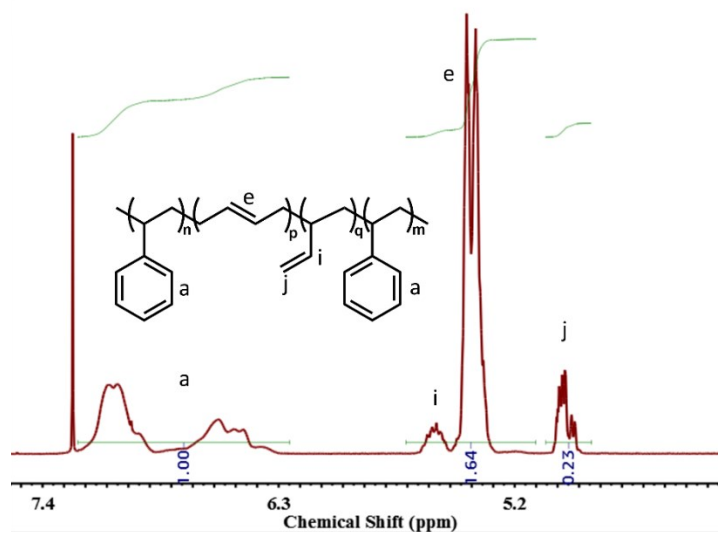**Figure S3.** Optical image of the star-like organogel after releasing stress.

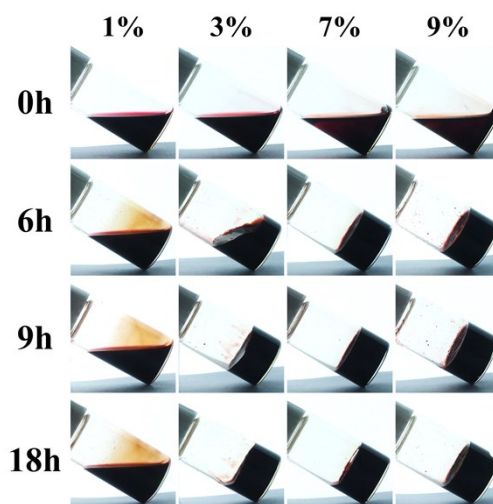**Figure S4**. ^{1}H-NMR spectrum of SBS and the integral of the corresponding peaks.

Figure S5. Optical images of the SBS solutions with different SBS concentrations under the ratio between double bonds to iodine at 2:1 and under different times. The concentrations of SBS solutions in chloroform were 1%, 3%, 7%, and 9% which represent 10 mg/mL, 30 mg/mL, 70 mg/mL and 90 mg/mL, respectively.
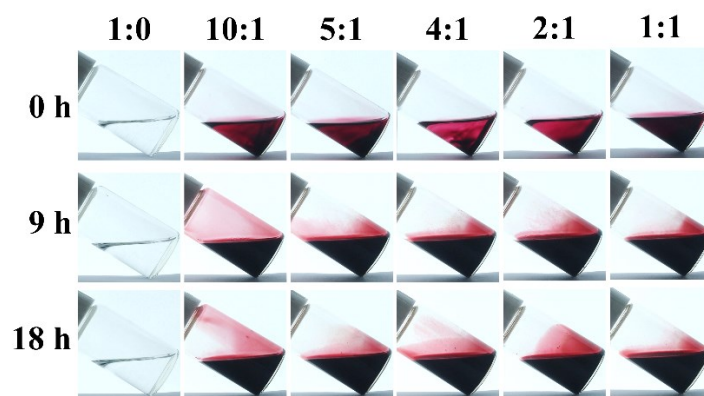
Figure S6. Optical images of the SEBS solutions with different iodine contents and under different times. 1:0 represents the pure SEBS solutions in chloroform without iodine, and 1:0, 10:1, 5:1, 4:1, 2:1 and 1:1 represent the molar ratios which are the same as that with SBS when given the concentration of SEBS solutions at 50 mg/mL.
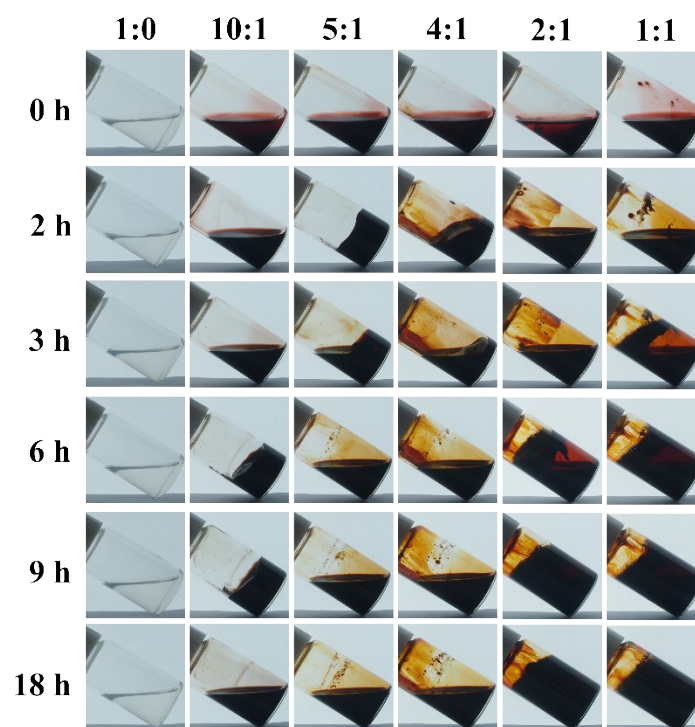

Figure S7. Optical images of the CPI solutions with different iodine contents and under different times.
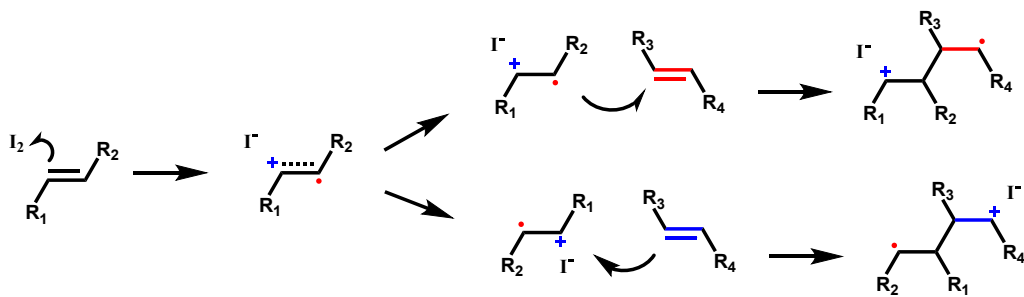
Figure S8. The proposed mechanism of the formation of SBS organogels.
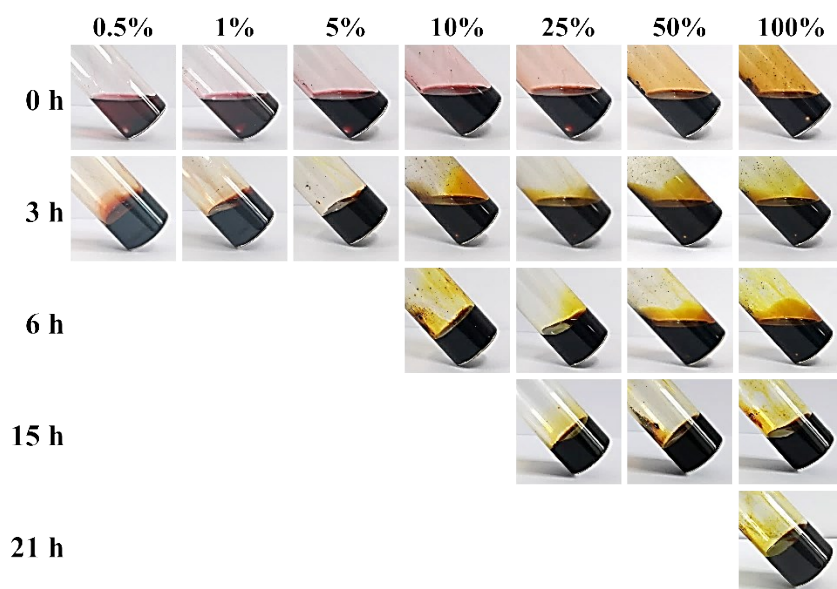

Figure S9. Optical images of the SBS solutions with different TEMPO concentrations under the ratio between double bonds to iodine at 2:1 and under different times. The concentrations of TEMPO were 0.5%, 1%, 5%, 10%, 25%, 50%, and 100% which represent the molar ratios of TEMPO to iodine.
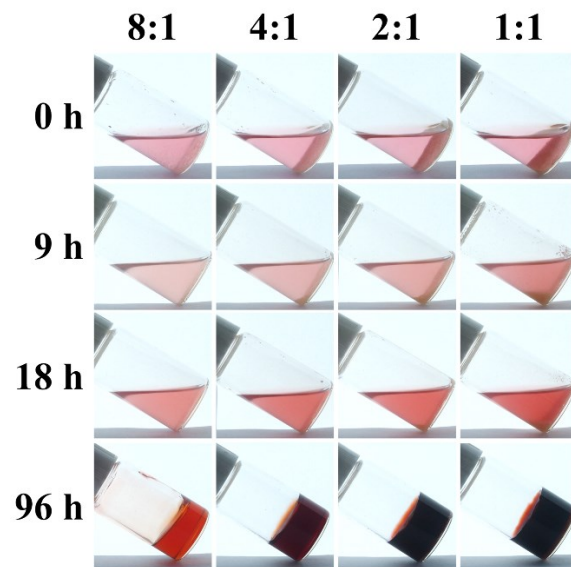
Figure S10. Optical images of the SBS solutions with different NIS contents and under different times.
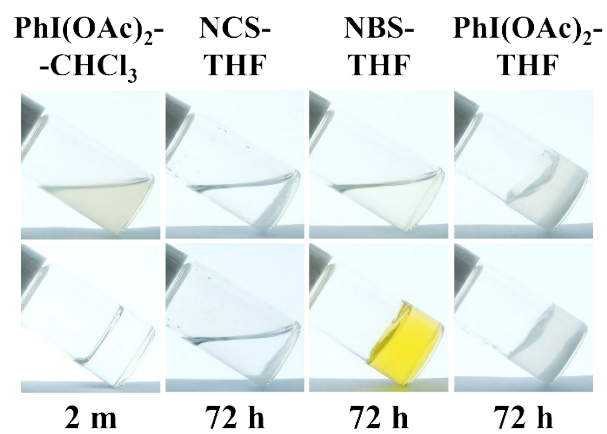

Figure S11. Optical images of the SBS solutions with different dopants under different times, the molar ratios between the double bonds and the dopants were 2:1.
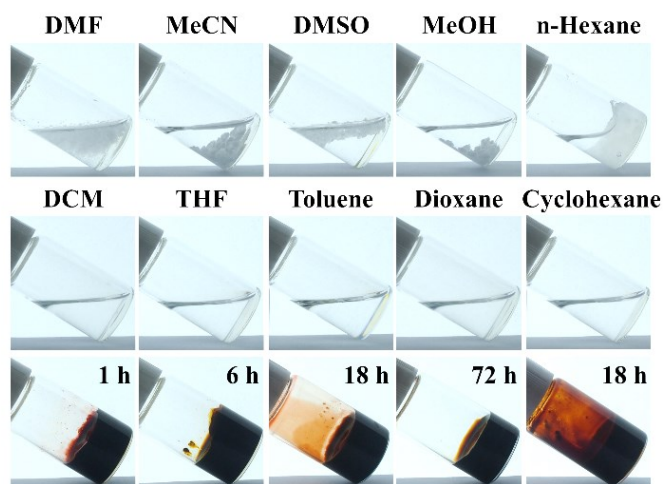
Figure S12. Optical images of the SBS solution with different solvents dissolved for 24 h. SBS could not be dissolved in DMF, MeCN, DMSO, MeOH and n-hexane, but can be dissolved in DCM, THF, toluene, dioxane and cyclohexane. The molar ratios between the double bonds and the iodine were 2:1.