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New application of Krafft point concept: An ultraviolet-shielded surfactant switchable window

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Table S2. Krafft Points of $Mg(DS)_2$, SLS and SDBS in EG-H_2O solvents.

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Movie S2. Transformation of Smart Window in the afternoon on November 23, 2018.

1. Materials and Methods

1.1 Materials

Acrylamide (AAm, 99.0%), N,N′-methylenebis-(acrylamide) (MBA, 99.0%) and N,N,N′,N′-tetramethylethylenediamine (TMEDA, 99.5%) were supplied by J&K (Beijing, China). Ammonium persulfate (APS, 99.99%), 2-(3,5-Di-tert-amyl-2-hydroxyphenyl) benzotriazole (98.0%), 2-(2H-benzotriazol-2-yl)-4-(1, 1, 3, 3-tetramethylbutyl) phenol (98.0%), the anionic surfactants: sodium dodecyl sulfate (SDS, 99.0%), sodium lauryl sulfonate (SLS, 99.0%), sodium dodecylbenzene sulfonate (SDBS, 99.0%) and magnesium dodecyl sulfate ($Mg(DS)_2$, 95.0%), were obtained from Aladdin (Shanghai, China). Ethylene glycol (EG) was supplied by Sinopharm (Shanghai, China). The UV absorbents, 2-hydroxy-4-(octyloxy) benzophenone (99.0%), 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (99.0%), 2,4-dihydroxybenzophenone (2,4-DHBP) and 2-hydroxy-4-methoxy- benzophenone (2H4MBP) were purchased from Macklin (Shanghai, China). The deionized water with the resistivity of 18.2 MΩ·cm (25 °C) was obtained from UPH-IV ultrapure water apparatus (China). All reagents were used directly without further purification.

1.2 Methods

1.2.1 Preparation of gels

The PAAm-SDS thermo-responsive hydrogels were synthesized by polymerization of AAm as monomer and MBA as crosslinking agent in SDS solution of EG and water mixed solvents. The hydrogels were named as PAAm-SDS-EGX hydrogels, where X is the number, representing the weight proportion of EG in mixed solvents. The preparation of PAAm-SDS-EG0 is introduced as an example: AAm (1.0 g), MBA (0.002 g), TEMED (0.03 g) and SDS (0.5 g) were added to 10 mL deionized water. The solution was sonicated at 100 Hz in an ultrasonic cleaner for 15 min to promote the dissolution. After the complete dissolution, 0.0159 g initiator, APS, was added. The solution was ultrasonically shaken at 100 Hz for 1 min and then the uniformly mixed solution was kept at 50 ^{o}C for 0.5 h.

1.2.2 Measurements and characterizations

The gel was operated with solvent exchange by ethanol for 24 h and then freeze-dried at -60 ^{o}C for 24 h to obtain the xerogel powders. Scanning electron microscopy (SEM) characterizations were observed on a Zeiss G300 SEM operating at 1 kV. Differential scanning calorimetry (DSC) measurements were performed on a Tzero 250 within the temperature of -20 - 70 ^{o}C and with a heating rate of 5 ^{o}C·min^{-1}.

1.2.3 Absorbance and transmittance measurements

The transmittance spectra in the wavelength range of 250 - 2500 nm were collected on a UV-visible-NIR spectrophotometer (Agilent Cary 5000, American) at normal incidence. The spectrophotometer was equipped with a heating and cooling stage. The integral luminous transmittance, T_{lum} (380-780 nm) were calculated by Eq. S1:[1]

$$T_{\text{lum}} = \frac{\int \varphi_{\text{lum}}(\lambda) T(\lambda)\, \mathrm{d}\lambda}{\int \varphi_{\text{lum}}(\lambda)\, \mathrm{d}\lambda} \qquad (1)$$

where $T(\lambda)$ denotes the spectral transmittance, $\varphi_{\text{lum}}(\lambda)$ is the standard luminous efficiency function of photopic vision in the wavelength range of 380 - 780 nm for an air mass 1.5. The $\varphi_{\text{lum}}(\lambda)$ is obtained at the sun standing 37º above the horizon with

1.5 atmosphere thickness, which corresponds to a solar zenith angle of 48.2º.[2] ΔT_{lum} is obtained by Eq. S2:

$$\Delta T_{lum} = T_{lum,20\,°C} - T_{lum,4\,°C} \qquad (2)$$

1.2.4 Adhesive properties of gels

The lap shear tests were performed according to the procedure previously reported.[3] Clean glass slides with the size of 75 mm were used as substrates. The gel precursor solutions were injected between two slides and gelled at 50 °C for 15 min. The overlapped area was set at 25 mm × 25 mm × 1 mm. Tests were performed by using a universal testing machine (TMS-PRO, American) with a crosshead of 20 mm·min^{-1} until the two glass slides were completely separated.

1.2.5 UPF, UV-A blocking and UV-B blocking calculation

The UV absorption of PAAm-SDS gels was further studied by UV spectra.[4] The UV protection factor (UPF) was calculated by Eq. S3:

$$\text{UV protection factor (UPF)} = \frac{\int_{280}^{400} E(\lambda)S(\lambda)\,\mathrm{d}\lambda}{\int_{280}^{400} E(\lambda)S(\lambda)T(\lambda)\,\mathrm{d}\lambda} \qquad (3)$$

where E (λ) is the relative erythema (skin redness) action spectrum, S (λ) is the spectral irradiance (W m^{-2} nm^{-1}), T (λ) is average spectral transmittance of fabric, d (λ) is bandwidth, and λ is wavelength.

The percentage blocking for UV-A (320-400 nm) and UV-B (280-320 nm) were calculated by Eqs. S4 and S5, respectively:

$$\text{UV} - \text{A blocking (\%)} = 100 - \frac{\int_{320}^{400} T(\lambda)\,\mathrm{d}\lambda}{\int_{320}^{400} \mathrm{d}\lambda} (\%) \qquad (4)$$

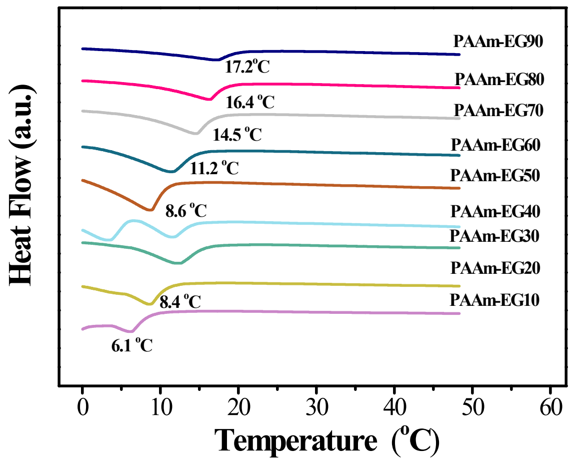
$$\text{UV-B blocking}(\%) = 100 - \frac{\int_{280}^{320} T(\lambda)\,\mathrm{d}\lambda}{\int_{280}^{320} \mathrm{d}\lambda}(\%) \tag{5}$$

By calculation, the UPF of the PAAm-SDS-EG80-UV gel is 722 with UV-A and UV-B blocking being 97.92% and 99.99%, respectively. According to the standard,[5] a product with a UV protection factor (UPF) larger than 40 (UPF 40+) and an average UVA transmission lower than 5% can be named a UV protection product.

1.2.6 UV-shielding ability of gels observation

The time that the gels can effectively block UV light was explored. Two UV detection cards, one covered by PAAm-SDS-EG80-UV gel and one being bare, were placed on a balcony to be continuously exposed to sunlight for average 12 hours per day. After the initial 15 days, the card covered by gel kept an unchanged state, but the bare card became purple under the sunlight and turned back to the initial white color at night. After the second 15 days, the card exposed to sunlight was found to become pale, losing the ability to change color. The card protected by PAAm-SDS-EG80-UV gel could still respond to sunlight. On the 73rd day, the gel lost its UV-shielding ability. The card turned purple under sunlight and lost the responsiveness to sunlight on the 100th day. In a word, the PAAm-SDS-EG80-UV gel can effectively block UV light for 73 days and its UV-shielding ability can be strengthened if the content of UV absorbents increases.

2. Supplementary Figures, Tables and Movies



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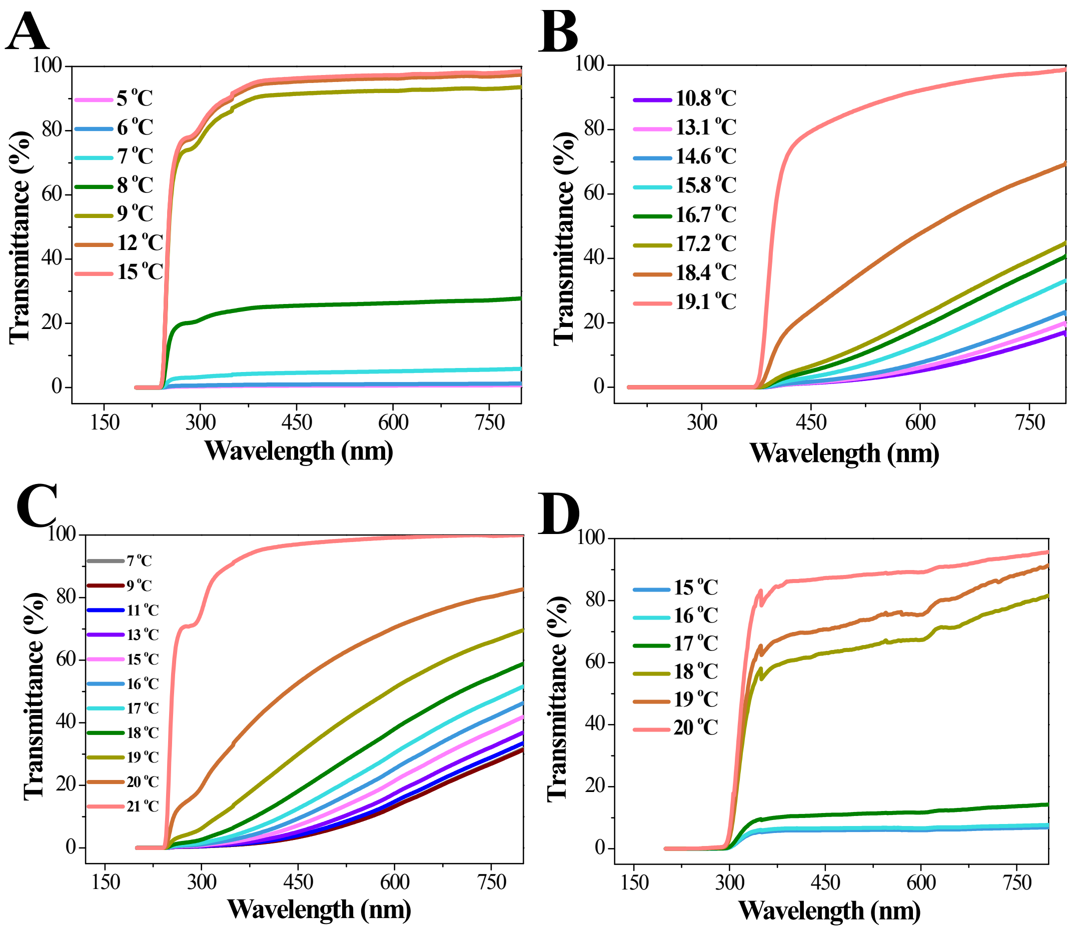

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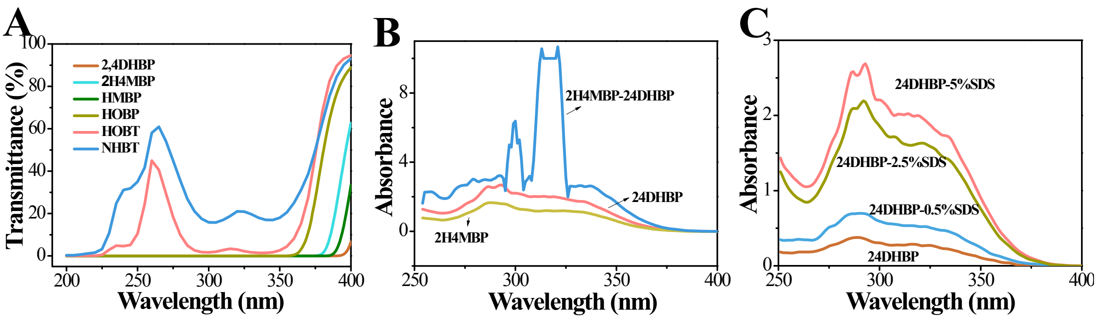

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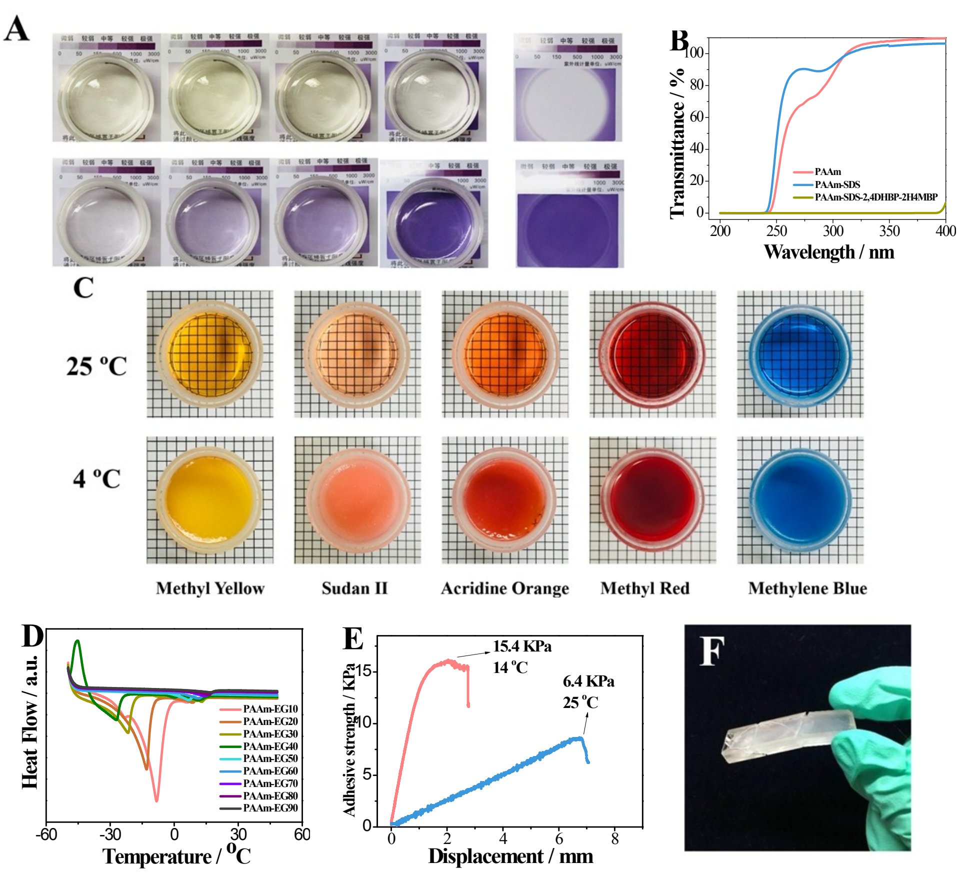

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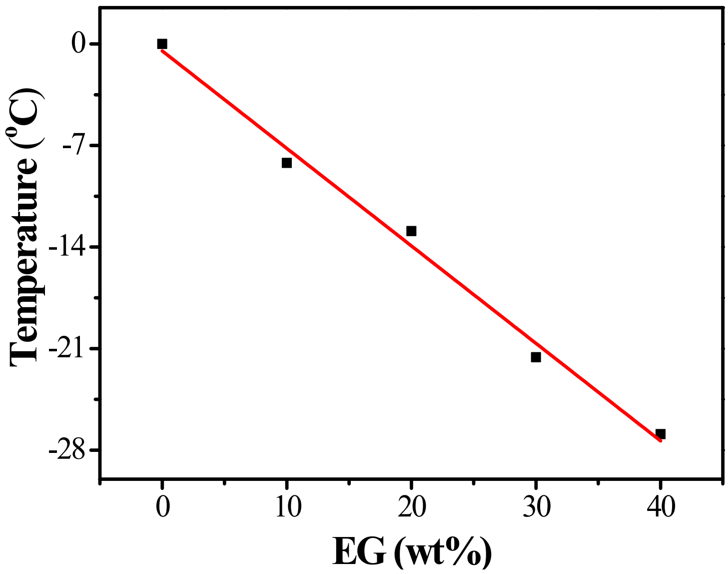

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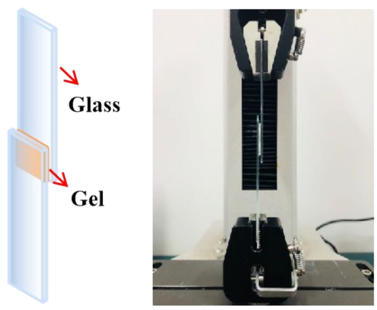

Fig. S6. The Photo of the lap shear tests.

Table S1. Recipes of the PAAm-SDS gels.

Samples	EG (wt%)	H_2O (wt%)	AAm (wt%)	MBA (mM)	Freezing points (ºC)
PAAm-EG0	0	100	10	1.3	0
PAAm-EG10	10	90	10	2.6	-8.2
PAAm-EG20	20	80	10	2.6	-12.9
PAAm-EG30	30	70	10	2.6	-21.6
PAAm-EG40	40	60	10	3.9	-26.9
PAAm-EG50	50	50	10	5.2	< -50
PAAm-EG60	60	40	10	6.5	< -50
PAAm-EG70	70	30	10	9.1	< -50
PAAm-EG80	80	20	10	10.4	< -50
PAAm-EG90	90	10	10	13	< -50

The samples consist of SDS (5 wt%), 2,4-DHBP (90 mM), KPS (7 mM), and TMEDA (7 mM) besides the reagents above.

Table S2. Krafft Points of $Mg(DS)_2$, SLS and SDBS in EG-H_2O solvents.

Ethylene Glycol (wt%)	Magnesium Dodecyl Sulfate (ºC)	Sodium Lauryl Sulfonate (ºC)	Sodium Dodecylbenzene Sulfonate (ºC)
0	32	32	48
10	30	33	53
20	28	36	55
30	26	38	56
40	23	40	60
50	22	41	63
60	-	42	65
70	-	44	68
80	-	47	70
90	-	50	75

Notes and references

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