Supporting Information

A light-switchable polymer adhesive based on photoinduced reversible solid-to-liquid transitions

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Materials

All chemicals and solvents were purchased from Sigma Aldrich or TCI Europe and were used without further purification. Quartz substrates and frosted quartz substrates (Hiraoka Special Glass, 15 × 48 mm, 1.5 mm thickness) were purchased from Chutian Co., Ltd. The azopolymer P1 was synthesized according to our previous work (Fig. S1)[1].

The azobenzene groups in the as-prepared spin-coated film were in a stable trans state and exhibited a strong π–π* band at ~336 nm. After UV irradiation, the π–π* band of the trans isomer decreased, and the n–π* band of the cis isomer at 450 nm increased (Fig. S2a). Subsequent visible light irradiation of the cis-rich P1 film switched it back to the trans state (Fig. S2b). The results demonstrate that alternating UV and visible light irradiation induced reversible photoisomerization (Fig. S2c, d). The cis content of the azopolymer film after UV irradiation was estimated according to a method in the literature[2,3].

Cis content = $(1-A/A_{trans})/(1-\varepsilon_{cis}/\varepsilon_{trans})$

where A is the absorbance of the azopolymer, A_{trans} is the absorbance of the trans polymer, and ε_{cis} and ε_{trans} are the molar absorption coefficients of the cis and trans isomers, respectively, at 336 nm. $\varepsilon_{cis}/\varepsilon_{trans}$ for azobenzene is close to 0.05[2,3]. The cis content was ~70% after UV irradiation.

Characterization

Adhesive lap joint shear strength tests were performed on a Zwick/Roell Z005 universal testing machine. UV-vis absorption spectra were recorded on a Lambda 900 spectrometer (Perkin Elmer). Trans-to-cis and cis-to-trans photoisomerization of the azopolymers were induced by LEDs at λ = 365 and 530 nm, respectively (device types LCS-0365-07-22 and LCS-0530-15-22, Mightex Systems). The output power of the LEDs was controlled by an LED controller (device type SLC-MA04-MU, Mightex Systems). Scanning electron microscopy (SEM) images were obtained on a LEO Gemini 1530 system. Contact angles

were measured with a contact angle meter, Dataphysics OCA35 (Data Physics Instruments GmbH, Germany). Optical microscopy (HAL 100) was used to observe the quarts surface after the lap joint shear strength tests, and the surface of different substrates.

Adhesion strength measurements

Adhesive lap joint shear strength tests were performed on a Zwick/Roell Z005 universal testing machine equipped with a 1 kN load cell and mechanical gripping clamps at room temperature. Two quartz substrates were glued together with P1 (thickness: ~1 µm) over an overlap area of 0.375 cm^2. The construct was mounted on the universal testing machine and pulled until failure at a strain rate of 0.2 mm/min. The maximum force was determined via the average value of the three measurements. Finally, the adhesion strength (in MPa) was determined by dividing the maximum force by the overlap area.

The breaking adhesion strengths were determined using a HANDPI NK-200 force gauge. Two quartz substrates were glued together with P1 over an overlap area of 0.75 cm^2. Typically, one side of the P1-glued substrate was fixed to a laboratory steel stand, while the other side was fixed to the force gauge. The breaking adhesion strength was measured by pulling the force gauge in the horizontal direction until the substrates were separated. At the same time, the force gauge recorded the force.

The reuse of P1 was also investigated using the force gauge. For the light-assisted process, trans-P1-glued substrates were separated by mechanical force and then irradiated with UV light (365 nm, 71 mW/cm^2, 15 min) to liquefy P1. Afterwards, the substrates were fixed together under pressure. The samples were irradiated with visible light (530 nm, 5 mW/cm^2, 15 min) to solidify P1. Reused trans-P1-glued substrates were prepared using the approach mentioned above, and the adhesion strength was measured using the force gauge.

Reused cis-P1-glued substrates were prepared by irradiating trans-P1-glued substrates with UV light. The adhesion strength was also measured using the force gauge. For the

solvent-assisted process, 10 μL DCM was dropped onto the separated quartz substrates. The substrates were glued together and dried in a fume hood for 24 h.

To measure underwater adhesion, trans-P1-glued substrates were prepared under dry conditions as mentioned above. The tensile tests were conducted after trans-P1-glued substrates were completely immersed in water. The substrates were separated by pulling in the opposite direction. The adhesion was measured using the force gauge. To study the underwater adhesion of cis-P1-glued substrates, the separated substrates in water were irradiated with UV light (365 nm, 71 mW/cm^2, 15 min). Then, the quartz substrates were clipped. The film was re-adhered. The sample was irradiated with UV light (365 nm, 5 mW/cm^2, 15 min) again to ensure that P1 was in a cis-rich state. After that, the cis-rich substrates adhesion was measured using the force gauge. Afterwards, the sample was immersed in water, and the underwater adhesion was measured using the force gauge.

To test the reversibility of underwater adhesion, we prepared trans-1 and trans-2 samples. To prepare the trans-1 sample, two quartz substrates were separated in water and kept in the wet state. P1 on the substrates was liquefied by UV light (365 nm, 71 mW/cm^2, 15 min). Then, the substrates were clipped and illuminated with green light (530 nm, 5 mW/cm^2, 15 min) for a liquid-to-solid transition. The sample was immersed in water, and its underwater adhesion was measured using the force gauge. To prepare the trans-2 sample, two quartz substrates were separated in water, and the sample was dried in an oven at 40 °C for 24 h. Then, 10 μL of DCM was dropped on the surfaces of the substrates. The substrates were glued together by pressing with a load (50 g) and were then placed in a fume hood for 24 h. Afterwards, the trans-2 sample was immersed in water, and its underwater adhesion was measured using a force gauge. All adhesion strengths were measured at least 3 times, and the average values were determined.

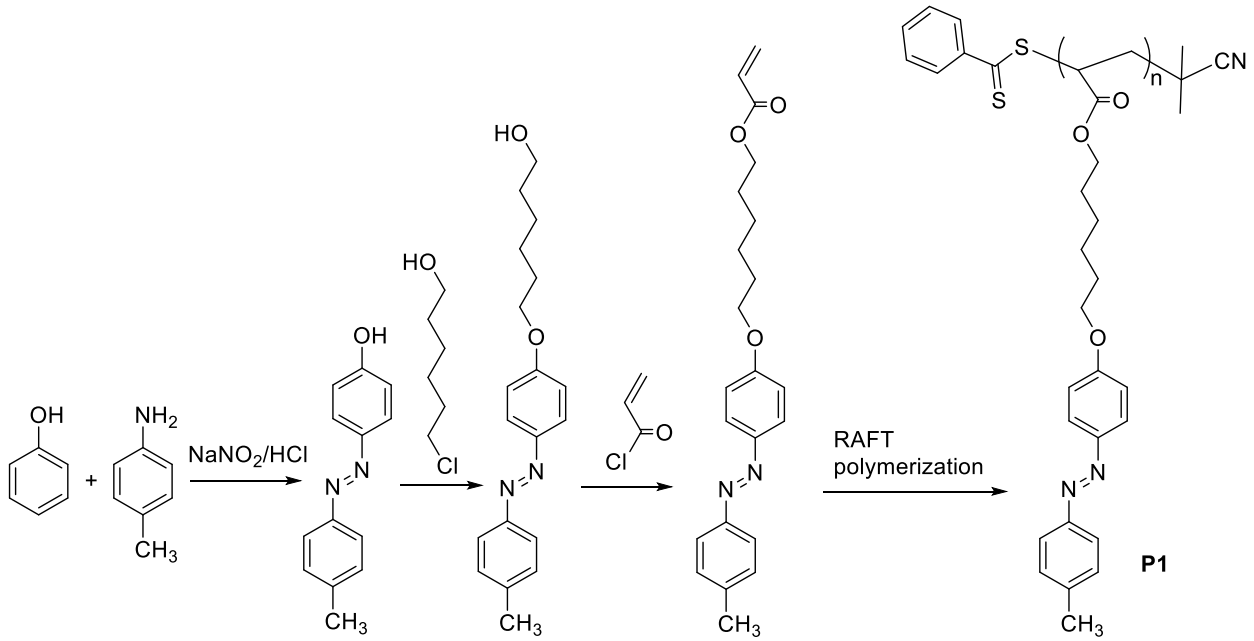

Fig. S1 Synthesis of the azopolymer P1.

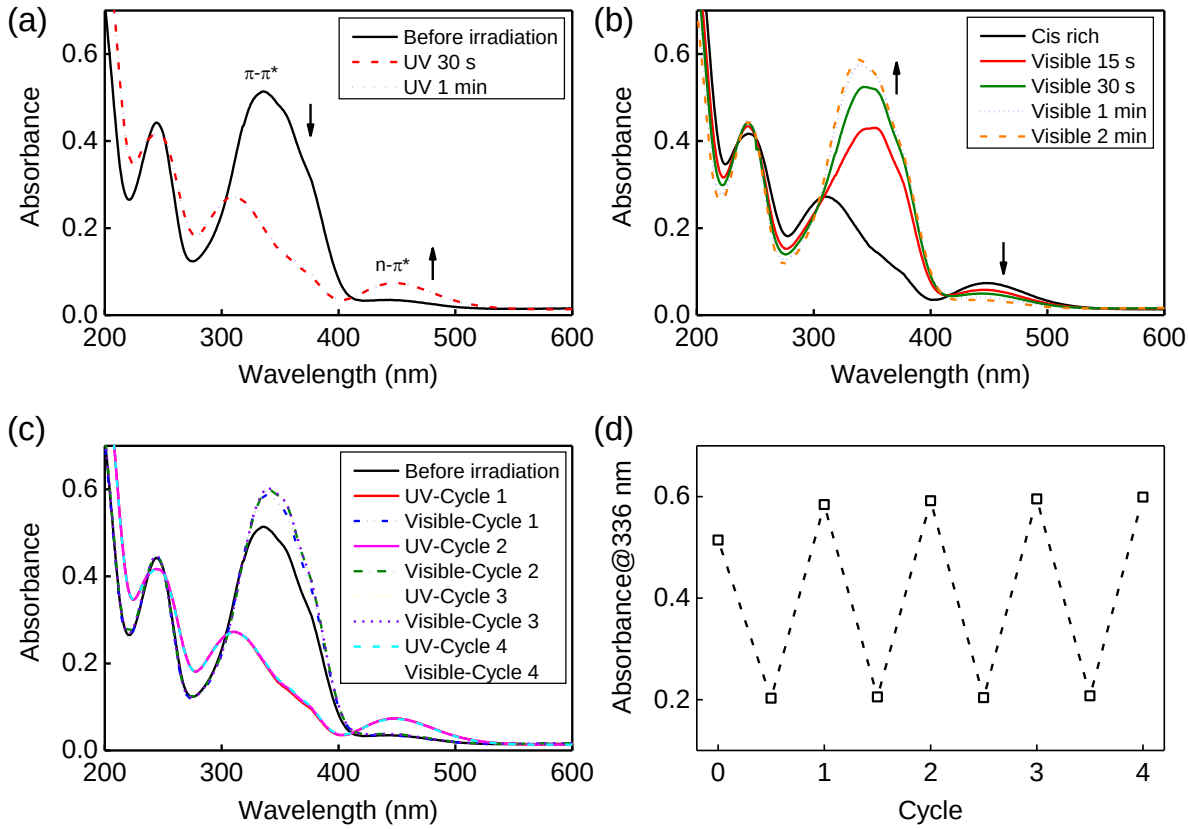

Fig. S2 Photoisomerization of P1 in a thin film. (a) UV–Vis absorption spectra of a trans P1 film before irradiation, and after 365 nm UV light (71 mW/cm^2) irradiation for 30 s and 1 min. (b) UV–Vis absorption spectra of the cis-rich P1 film after 530 nm visible light (5 mW/cm^2) irradiation for 15 s, 30 s, 1 min, and 2 min. (c) UV–Vis absorption spectra of a spin-coated P1 film before irradiation and after alternating UV (365 nm, 71 mW/cm^2, 1 min) and visible light (530 nm, 5 mW/cm^2, 2 min) irradiation. (d) Absorption changes under alternating UV and visible light irradiation.

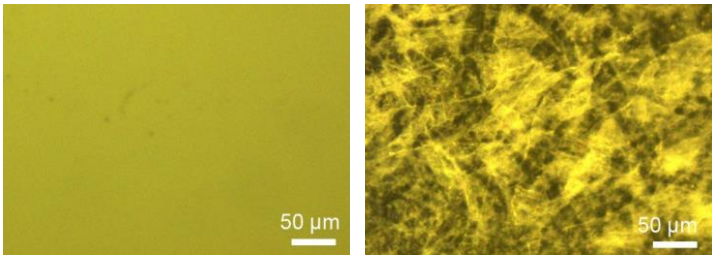

Fig. S3 Optical microscopy images of quartz and paper used for the experiments in Fig. 3b. The quartz had a flat surface. In contrast, the paper had a rough surface. The photo-liquified cis P1 filled the rough areas and penetrated into the paper, resulting in increase of the effective surface areas.

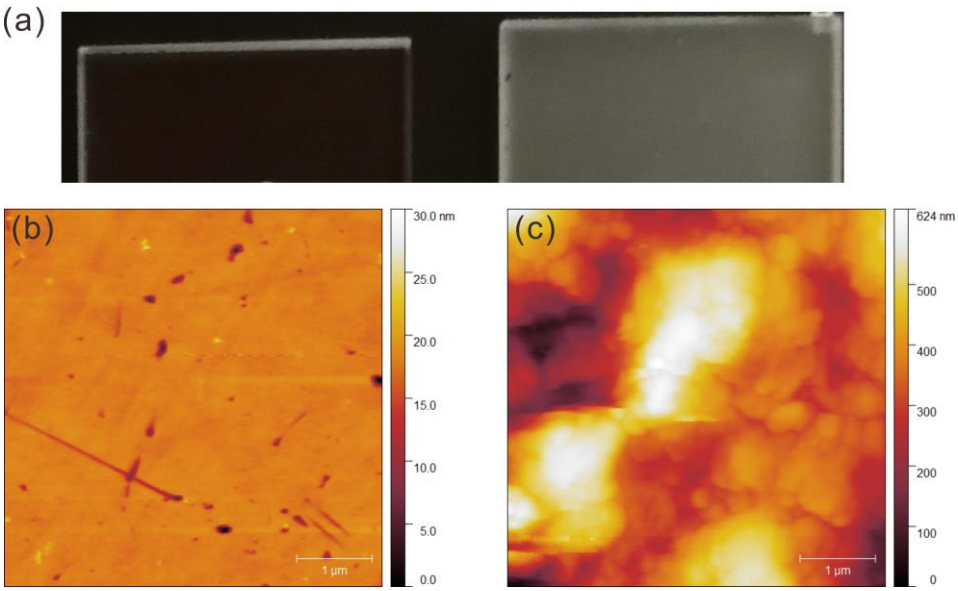

Fig. S4 (a) Photograph of flat (left) and frosted (right) quartz substrates. AFM images of (b) flat quartz and (c) frosted quartz. The root mean square (RMS) roughnesses of the flat and frosted quartz substrates measured by AFM are 0.9 nm and 111.2 nm, respectively.

Movie S1. Light-controlled adhesion. Trans-P1-glued substrates lifting a bottle of water (~ 500 g). UV light induced trans-to-cis isomerization and reduced adhesion. The bottle fell. The bottle of water on the right side is a control sample.

Movie S2. Light-controlled underwater adhesion. Trans-P1-glued substrates lifting a copper block (~2.6 kg). UV light induced trans-to-cis isomerization and reduced adhesion. The copper block fell after light irradiation.

References

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