

Rapid Photoresponsive Switchable Pressure-Sensitive Adhesive Containing Azobenzene for the Mini-Light Emitting Diode Transfer Process

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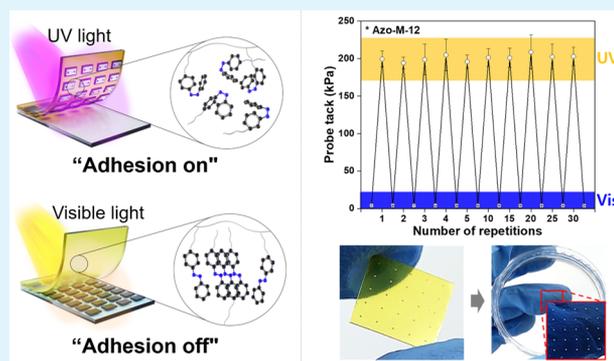
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ABSTRACT: Materials that can switch adhesive properties based on external stimuli are required in several industries for temporary bonding or transfer processes. Previously studied materials achieve this under restricted conditions (hydration, heat, and long switching times), and some materials have limitations related to reuse because of irreversible reactions or residue formation on substrates. Herein, a rapid photoresponsive switchable pressure-sensitive adhesive (PSA) fabricated using an acrylic polymer and an aliphatic monomer containing azobenzene is reported. The adhesion force of the proposed PSA can be switched by photoisomerizing the azobenzene moiety. The process induces the transition of surface energy and modulus of the PSA. Ultraviolet and visible light irradiation can switch the probe tack force from 200 to 4 kPa within 15–30 s. Adhesion switching is possible in a state wherein the PSA remains adhered to a substrate. Mini-LEDs are selectively transferred from the carrier PSA to a polydimethylsiloxane substrate following the process of partial adhesion switching of the PSA. The novel and switchable PSA, which exhibits a selective and repeatable adhesion switching property and high switching ratio when stimulated by light stimuli, may be potentially used to realize the mini-LED or micro-LED transfer processes.

KEYWORDS: pressure-sensitive adhesives, photoresponsive, switchable, azobenzene, mini-LEDs



1. INTRODUCTION

Pressure-sensitive adhesives (PSAs) are different from conventional adhesives in terms of the adhesion mechanism. PSAs do not require the influence of heat, presence of a solvent, or a phase change to adhere to the substrate at room temperature.¹ This advantage allows PSAs to be used for attaching dissimilar substrates, which has extended their applicability to areas beyond those related to daily life and general industrial use in automobile, electrical and electronic, and biomedical industries.^{2,3}

The adhesive strength of PSAs is related to their surface energy and physical property.⁴ Therefore, the adhesive strength is kept constant in a fixed environment (where the temperature, humidity, and detaching rate are kept constant) because the surface energy and physical property are determined when the PSA is formed. Recently, adhesives with controllable adhesive properties have found their applications in the electrical, electronics, and medical industries. The properties of these materials allow them to get easily released from the surface based on user demands even if the adhesives were well attached to the substrates before being released. Such PSAs are called dynamic adhesives⁵ or switchable adhesives.⁶ Croll *et al.* defined switchable adhesives as materials that exhibit adhesion

switching by changing the contact area, interfacial property, and material compliance.⁶

Many researchers have studied stimuli-responsive materials. Mechanisms that enable switching include reversible host–guest interactions,^{7,8} transition of coordination complexes with metal ions,^{9–11} conformational transition of polymers,¹² hydrogel swelling using water,¹³ transition of the crystalline structure of liquid crystal elastomers,^{5,14–16} photoisomerization of azobenzene moiety,^{8,17} and irreversible cross-linking.^{18,19} External stimuli (e.g., mechanical, thermal, and electromagnetic) that enable switching are called switching triggers.⁶ These include heat,^{5,14–16} solvents,²⁰ water,¹³ pH control,^{7,12} and light.^{8,10,11,16–19} However, some of the abovementioned trigger systems only work in an aqueous environment or do not exhibit the property of repeatability. In addition, the heating process can damage the substrate, which affects its

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application. Therefore, we focus on developing a switchable PSA that can be used repeatedly in a dry state using light as the switching trigger.

Recently, displays manufactured using inorganic light-emitting diodes (LEDs; size: <100 μm) are being considered as the next-generation displays. Small inorganic LEDs are also known as mini-LEDs or micro-LEDs. Compared to conventional liquid crystal displays or organic LED displays, mini- and micro-LEDs exhibit higher contrast and have faster response times, a longer lifespan, and higher energy efficiency.²¹ However, they cannot be fabricated directly on the display panel and require the transfer of millions of individual LEDs to the panel.²² Transfer can be achieved using kinetically controlled polydimethylsiloxane (PDMS) stamps,^{23,24} thermal release films,²⁵ laser-driven processes,^{26,27} ultraviolet (UV) tapes,²⁸ and magnetorheological elastomers.²⁹ The kinetically modulated PDMS stamp is a representative transfer method that exploits the frequency dependence of the viscoelastic material to transfer devices by varying the speeds of the picking and releasing processes. However, the adhesive force can only be adjusted within a limited range. Surface contamination can hinder the process.³⁰ Moreover, it is not possible to selectively switch the property of adhesion. Other methods have limitations such as using heat stimuli that can damage the device, difficulty to reuse, and a narrow adhesion range. Thus, materials that exhibit selective adhesion switching, a wide modulation range, and reusability should be developed.

We used the azobenzene moiety (a representative photo-responsive unit) for designing a switchable PSA that satisfies the abovementioned conditions. Researchers have previously used the azobenzene moiety to develop switchable adhesives and achieve adhesion switching by exploiting the properties of hydrogel systems,⁸ phase transition,^{17,31–35} or softening.^{36,37} Early studies on switchable adhesives exploiting the properties of phase transition in the presence of azobenzene units were conducted using sugar alcohol derivatives containing a multi-azobenzene moiety.¹⁷ Later, studies using acrylic homopolymers^{31,34,35} or block copolymers^{32,36,37} with azobenzene side chains were conducted. These materials can be liquefied or softened by irradiating them with UV light. The process results in the loss of adhesive strength. However, liquefaction and softening-based debonding cannot be used to realize the LED transfer process because the residue can contaminate the device.

Therefore, we fabricated a switchable PSA using a mixture of acrylic polymer and aliphatic monomer (containing the azobenzene moiety). The adhesion property of this PSA can be “switched on” in the presence of UV radiation and “switched off” in the presence of visible (Vis) light radiation. The switching process does not proceed through the solid-to-liquid phase transition step. To the best of our knowledge, there are no reports on a switchable PSA whose adhesive strength can be repeatedly and selectively “switched on and off” for realizing the mini- or micro-LED transfer process under conditions of short light irradiation. We successfully realized an electronic device transfer process and transferred mini-LEDs from a carrier PSA to a PDMS substrate using the fabricated switchable PSA. The selective transfer was also achieved by partial adhesion switching using a photomask. Our novel and switchable PSA can be potentially used to realize the transfer process of mini-LEDs, micro-LEDs, microscale inorganic circuits, and semiconductors.

2. EXPERIMENTAL SECTION

2.1. Materials. 4-Phenylazophenol (PAP, 98%), dibutyltin dilaurate (DBTDL, 95%), and butyl acrylate (BA, >99%) were purchased from Sigma-Aldrich. Potassium carbonate (>99%), potassium iodide (>99.5%), 6-chloro-1-hexanol (>96%), and 1-chlorotetradecane (>98) were purchased from Tokyo Chemical Industry Co., Ltd. 2,2'-Azobisisobutyronitrile (AIBN, 98%), 2-butanone (MEK, 99.5%), and ethyl acetate (EA, 99.5%) were purchased from Samchun Chemicals Co., Ltd. *N,N*-Dimethylformamide (DMF, >99.5%) was purchased from Daejung Chemicals & Metals Co., Ltd. Karenz AOI (2-isocyanatoethyl acrylate, Showa Denko) was used as the isocyanate-containing acrylic monomer. Sylgard 184 (Dow Corning) was used as the PDMS acceptor in the mini-LED transfer test.

2.2. Synthesis of Azobenzene-Containing Monomers.
2.2.1. 6-(4-(Phenyldiazenyl)phenoxy)hexan-1-ol. The method used in Zhou's study was employed.³⁸ PAP (3.586 g, 0.018 mol) and potassium carbonate (2.488 g, 0.018 mol) were dissolved in DMF (15 mL) by stirring for 30 min at room temperature. Thereafter, potassium iodide (7.5 mg, 0.045 mmol) and 6-chloro-1-hexanol (3.689 g, 0.027 mol) were added to the PAP solution. The solution was stirred and kept at 110 °C for 24 h. The reaction mixture was poured into diethylether and washed with water three times. After drying diethylether with air, the residue was precipitated with water. The precipitate was dried at room temperature under a vacuum condition after filtering. The dried compound was washed with *n*-hexane to obtain a yellow powder; the yield was 76.11%.

2.2.2. 2-(((6-(4-(Phenyldiazenyl)phenoxy)hexyl)oxy)carbonyl)amino)ethyl Acrylate (Azo-Acrylate). 6-(4-(Phenyldiazenyl)phenoxy)hexan-1-ol (2.000 g, 0.007 mol) was dissolved in MEK (15 mL). 2-Isocyanatoethyl acrylate (1.976 g, 0.014 mol) was added to the solution, and the solution was stirred at 40 °C under an atmosphere of N_2 . Thereafter, DBTDL (0.019 g) was added to the solution. The temperature of the reaction mixture was maintained at 40 °C for 6 h. The reaction mixture was then poured into cold *n*-hexane (300 mL), and the mixture was filtered. This process was repeated three times. The filtered compound was dried at room temperature under vacuum to obtain the product; the yield was 84.01%.

2.2.3. 1-Phenyl-2-(4-(tetradecyloxy)phenyl)diazene (Azo-M). To synthesize Azo-M, the method for the synthesis of 6-(4-(phenyldiazenyl)phenoxy)hexan-1-ol was followed, but 1-chlorotetradecane was used instead of 6-chloro-1-hexanol. The yield was 48.64%.

2.3. Polymerization of the BA/Azo-Acrylate Copolymer (Azo Polymer). After removing the inhibitor of BA using neutral aluminum oxide, BA (1.5 g, 0.012 mol) and Azo-acrylate (0.572 g, 1.3 mmol) were added to EA (5 mL). After stirring the mixture for 1 min at 70 °C to dissolve the Azo-acrylate powder, N_2 gas was blown into the solution for 20 min at room temperature. AIBN (0.01 g) was added to the solution, and the solution was stirred at 70 °C for 1.5 h. Tetrahydrofuran (THF, 5 mL) was poured into the polymerized solution to prevent gelation caused by the interaction between the azobenzene moieties. The polymer solution was washed and dissolved with methanol and THF, respectively. The process was repeated thrice. The dissolved solution was poured on a silicone-release film and dried at 70 °C. The M_n , M_w , and polydispersity index (PDI) were 39,900, 147,400, and 3.8, respectively.

2.4. Preparation of the Switchable PSA Specimens. The dried azo polymer (0.1 g) was dissolved in THF (1 mL). Azo-M (4, 8, and 12 mol %) was added to the azo-polymer solution. The Azo-M content was calculated based on the number of all monomers present in the polymer. The solution was mixed using a vortex mixer. Thereafter, the solution was casted on a PET film (corona-treated, 50 μm) with a film applicator (wet thickness: 120 μm). The film was dried at 100 °C over 20 min in a convection oven. The thickness of the dried PSA was 6–7 μm measured with a digital micrometer (S-Mike Pro, Sylvac). The rigid-body pendulum-type physical properties testing (RPT), lap shear test, X-ray diffraction (XRD), and polarized optical microscopy (POM) specimens were casted on other substrates

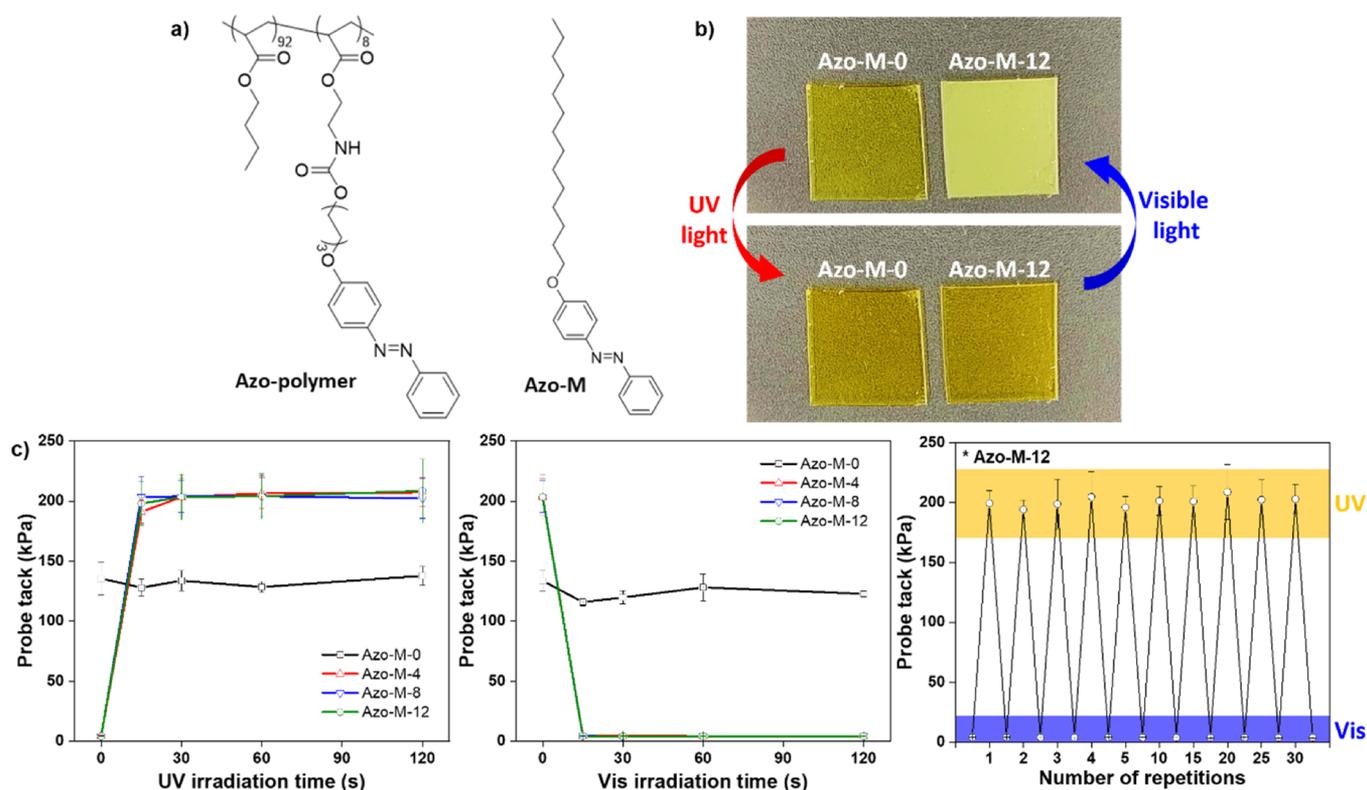


Figure 1. (a) Chemical structures of the azo polymer and Azo-M, (b) transmittance and color change of the switchable PSA in the presence of Azo-M upon photo-irradiation, (c) probe tack according to UV and Vis irradiation times and the adhesion switching repetitive test conducted with Azo-M-12.

following the method previously mentioned (RPT: steel plate; lap shear test: silicone-release film; XRD and POM: slide glass).

2.5. Preparation of the PDMS Acceptor. The PDMS resin and curing agent (resin:curing agent = 10:0.5) were mixed using a paste mixer (ARE-310, Thinky) operated at 2000 rpm. The process was allowed to proceed for 3 min (mixing: 2 min, deforming: 1 min). The mixture was poured into a petri dish and the sample was cured at 80 °C (curing time: 12 h).

2.6. Characterization. The nuclear magnetic resonance (NMR) spectra were recorded using a 400 MHz NMR spectrometer (JNM-ECX400, JEOL) operated at room temperature. Tetramethylsilane ($\delta = 0$ ppm) was used as the reference for determining chemical shift.

A 365 nm LED UV lamp was used for UV irradiation (intensity: 120 mW/cm²). A 50 W white LED lamp was used to irradiate Vis light to the samples. UV was irradiated from the direction in which the PSA surface was exposed. Meanwhile, Vis light was irradiated to the backside of the film to avoid the shading of the attached substrate.

The probe tack and peel strength were measured using a texture analyzer (TA.XT plus, Stable Micro Systems) at 25 °C (RH: 50 ± 10%). A cylindrical probe (stainless steel, diameter: 5 mm) was used for the probe tack test. After the probe was in contact (100g_f) for 1 s, it was detached at a speed of 10 mm/s. The test speed for the peel test was 5 mm/s, and the test angle was 180°. The width of the PSA specimen was 10 mm. The specimen was attached to a silicon wafer substrate by applying pressure using a 2 kg rubber roller. All experiments were repeated five times and the average value was used.

The adhesion switching test in the video (Supporting Information) was conducted as a 90° peel test. The silicon wafer was used as the substrate for the test. The 2 kg rubber roller was also used to attach the PSA specimen with a width of 10 mm to the substrate. Two small-sized binder clips (2.5 g each) were applied to the ends of the PSA specimen.

The UV/Vis absorption spectra were recorded using a UV/Vis spectrometer (OPTIZEN Alpha, K LAB). The wavelength scan range was between 200 and 700 nm. The 50 μm PET film used as the

backing film of the PSA was considered the baseline of the spectrum. The PSA was then measured as it was coated on the PET film.

The logarithmic damping ratio of the switchable PSAs was measured following the RPT (RPT-3000 W, A&D Company) method. The rigid-body pendulum and edge were FRB-400 and a round type (RBP-040). The pendulum weight, including the edge, was 109 g. The steel plate coated with switchable PSAs was placed on a specimen mount. After putting the pendulum on the surface of the PSA, the lower part of the pendulum containing a magnet was attracted to 0.1° for 2 s by magnetic force. After removing the magnetic force, the pendulum oscillated freely, and the attenuation of the amplitude was detected for 8 s by the displacement sensor. The sequence, attraction and oscillation, was recorded repeatedly for 5 min. The reduction of the amplitude was used for calculating the logarithmic damping ratio (Δ) as

$$\Delta = [\ln(A_1/A_2) + \ln(A_2/A_3) + \ln(A_3/A_4) + \dots + \ln(A_n/A_{n+1})]/n \quad (1)$$

where A denotes the amplitude and n denotes the number of oscillation waves.³⁹

The shear modulus was measured by conducting a lap shear test using dynamic mechanical analysis (DMA, Q800, TA Instruments). The size of the poly(methyl methacrylate) (PMMA) substrate was 6 mm × 20 mm × 1 mm (width × length × thickness), and the adhesion area was 6 mm × 10 mm (width × length). The thicknesses of PSAs casted on the silicone-release film were 6–7 μm measured with the digital micrometer. The PSA was attached between two PMMA substrates after UV irradiation. A shorter PMMA (6 mm × 6 mm × 1 mm) was attached to the end of each substrate using instant adhesive. For testing the Vis-irradiated specimen, Vis light was irradiated through the transparent PMMA substrate. The test was conducted using the strain ramp mode of DMA at 25 °C. The test speed was 1%/s. All measurements were taken three times and the average value was used.

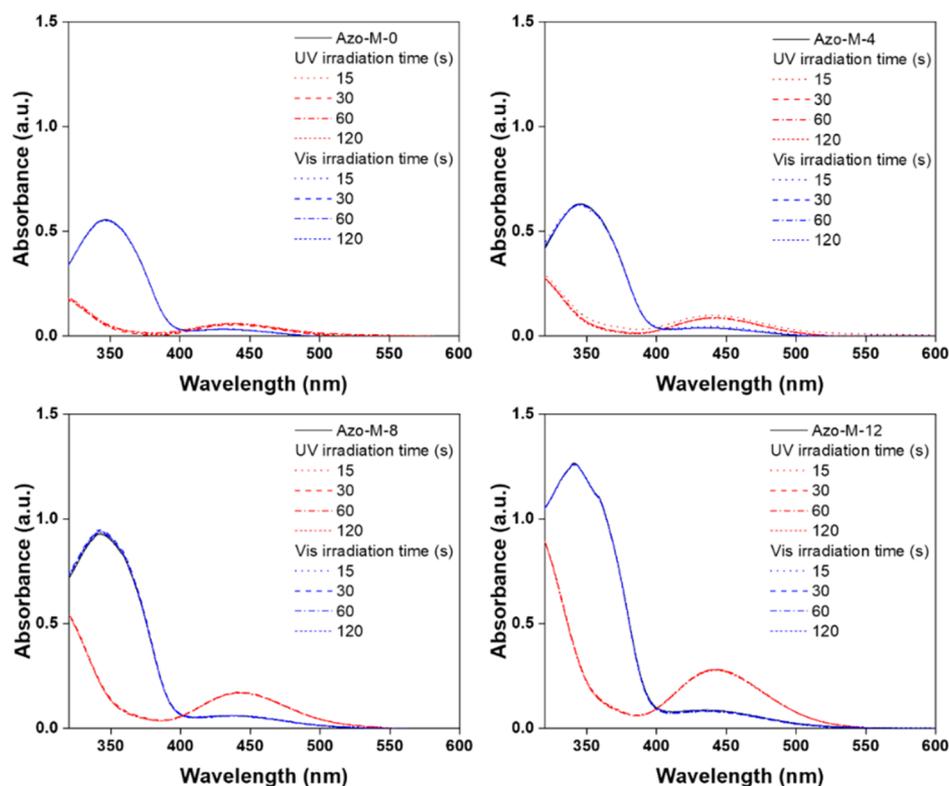


Figure 2. UV/Vis absorption spectral profiles of the switchable PSAs for observing the photoisomerization of the azobenzene moiety.

The water contact angle was measured using a drop shape analyzer (DSA 100, Krüss). It controlled the water volume at 5 μL . The contact angle was measured 10 s after dropping the water sample. Measurements were taken five times (for each specimen) and the average value was used.

The XRD patterns of the switchable PSA and Azo-M were recorded using a high-resolution XRD machine (Rigaku SmartLab; Cu $K\alpha$ radiation) in the range of 5–40° at 25 °C. The differential scanning calorimetry (DSC) curve was obtained using a Q200 DSC (TA Instruments). After heating to 250 °C, the data were recorded when the sample was cooled to 0 °C and reheated at 10 °C/min.

3. RESULTS AND DISCUSSION

We polymerized the azo polymer with an acrylic monomer containing azobenzene and BA. The azo polymer was washed using methanol. The mole ratio was calculated by analyzing the ^1H NMR spectrum of the azobenzene moiety remaining in the polymer chain. The mole percentage was calculated to be 8 mol % (Figure S4). We synthesized the azobenzene monomer (Azo-M) containing a long aliphatic chain. The switchable PSA was prepared by blending the azo polymer with Azo-M (Figure 1a). The switchable PSAs were named based on the Azo-M content (Azo-M-0, Azo-M-4, Azo-M-8, and Azo-M-12). The transparent azo-polymer film became opaque when Azo-M was added. The film containing Azo-M became transparent after UV irradiation. Both films appeared dark yellow after UV irradiation (Figure 1b). Changes in the optical properties and stickiness of the surface were observed, but phase transition (between the solid and liquid phases) was not observed.

The probe tack was measured to determine the adhesion switchability and switching time of the switchable PSA (according to the UV and Vis irradiation time). For Azo-M-0, the initial value was 136 kPa. This tack value could be maintained even when the UV irradiation time was increased

to 2 min (Figure 1c). Since only 4 mol % of Azo-M (Azo-M-4) was added, the initial probe tack was reduced to 4 kPa. The surface had a nonsticky film-like state. The tack value, which was close to 0, dramatically increased to 200 kPa when the sample was subjected to UV irradiation for a short time of 15 s. The value could be maintained (at 200 kPa) for 2 min. However, further changes in the maximum value and switching time were not observed even when the content of the Azo-M was increased. The Vis irradiation test was conducted after irradiating the sample with UV light for 30 s. Azo-M-0 exhibited no change in adhesion force even when it was irradiated with Vis light for 2 min. For the Azo-M-containing PSAs, the tack value reached the minimum value after 15 s of Vis irradiation. The initial value (4 kPa) was reached again. Further, we studied the repeatability of adhesion switching. The PSA could be switched between its on and off states up to 30 times. During the process, the minimum and maximum values did not change. In summary, a repeatable switch between the nonsticky film and sticky PSA states could be achieved by mixing the azo polymer with Azo-M. A high adhesion force (200 kPa) was achieved within a short UV irradiation time (switching time: 15–30 s).

Kendall defined the probe tack force (F) of an infinitely thick elastic material as follows:

$$F = \sqrt{\frac{8\pi}{(1-\nu^2)}E\omega a^3} \quad (2)$$

where ν denotes Poisson's ratio, E denotes Young's modulus, and ω denotes the work of adhesion when using a rigid probe of diameter $2a$.⁴⁰

Further, ω can be calculated as

$$\omega = \gamma_a + \gamma_s - \gamma_{as} \quad (3)$$

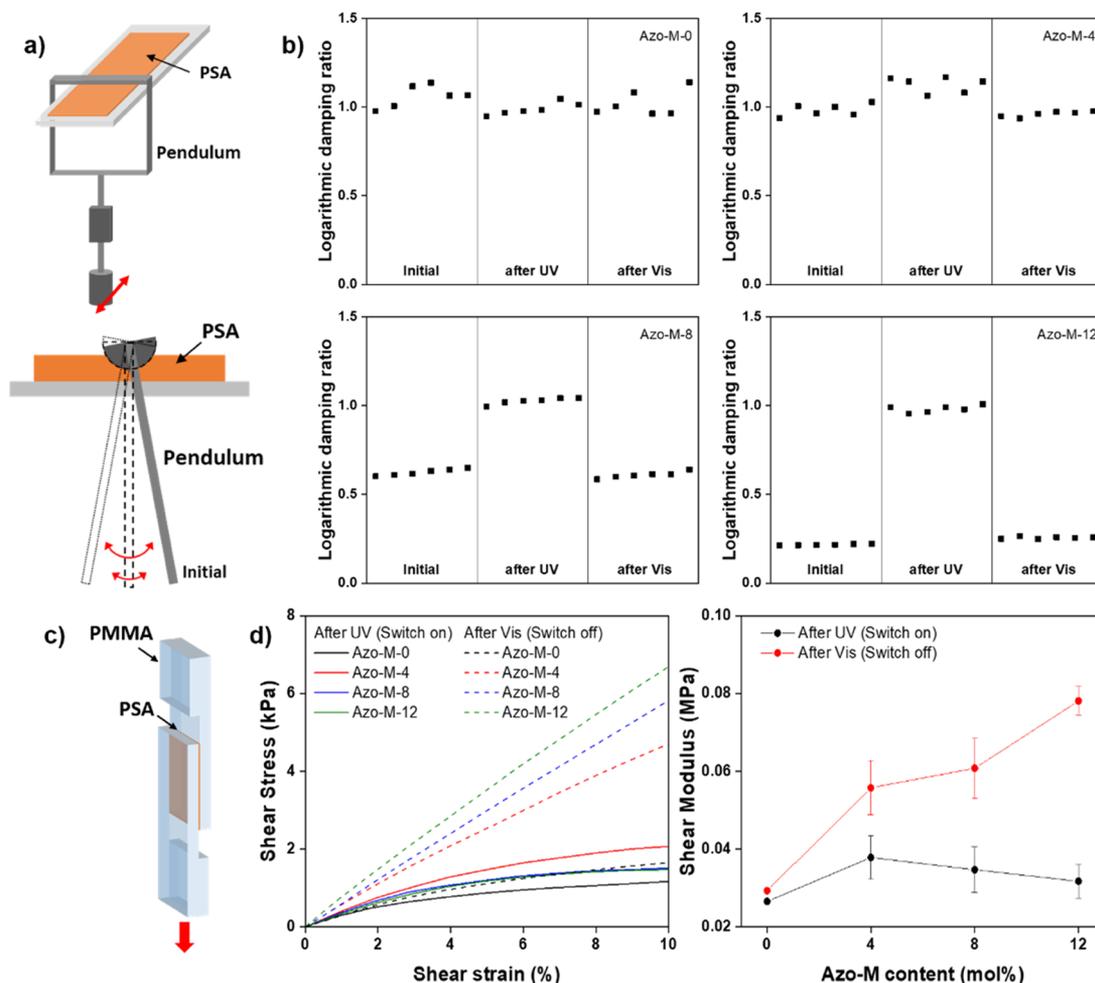


Figure 3. (a) Schematic representation of the RPT measurement method, (b) logarithmic damping ratio of the switchable PSAs obtained through the RPT, (c) schematic representation of the lap shear test specimen, (d) changes in the lap shear stress and modulus of the switchable PSAs with UV and Vis irradiation.

where γ_{ad} , γ_{st} , and γ_{as} denote the surface energy of the adhesive, substrate, and interface (of the adhesive and substrate), respectively. Based on eq 2, a change in the modulus and chemical characteristics of the PSA can cause a change in the adhesion force if external conditions such as temperature, thickness, adhesion area, and test speed are kept constant. Therefore, we studied the modulus and chemical characteristic transition of the switchable PSA in the presence of a photostimulus.

We used UV/Vis spectroscopy to observe the photoisomerization occurring in the PSA during UV and Vis irradiation. We expected that the photoisomerization of the azobenzene moiety could lead to the physical and chemical transitions in the switchable PSA. The stable *trans*-azobenzene moiety has a strong absorption band near 350 nm due to the transition from the bonding (π) orbital to the antibonding (π^*) orbital. Meanwhile, the isomerized azobenzene moiety to the *cis*-form has a predominant absorption band at 440 nm due to the transition from the nonbonding (n) orbital to the antibonding (π^*) orbital.^{41,42} Even in the initial state of Azo-M-0, a spectrum corresponding to the *trans*-form is observed because of the azobenzene moiety present in the polymer chain. In other samples, the absorption intensity of the *trans*-isomer increased with an increase in the Azo-M content (Figure 2). There was little or no absorption (*cis*-form) in the

440 nm region in the initial state. Regardless of the Azo-M content, most *trans*-isomers were converted to the *cis*-form after only 15 s of UV irradiation. The trend of *cis*-to-*trans* isomerization caused by Vis irradiation was the same. When azobenzene groups form a highly ordered crystalline structure in a solid phase, the photoisomerization of azobenzene is difficult to achieve because the free volume is not sufficient.^{43,44} In this study, it is considered that butyl groups of the azo polymer and the long alkyl substituent of the Azo-M contributed to securing free volume that can cause rapid photoisomerization.

The influence of rapid photoisomerization on the physical characteristics of the PSAs was confirmed by the RPT and shear modulus evaluation. The RPT has been used for evaluating curing behavior and viscoelastic properties of polymer coating materials or adhesives.^{39,45–47} In this study, the RPT method is used to measure the viscoelastic properties of the PSA by detecting the attenuation of the amplitude of the pendulum via the displacement sensor after oscillating the pendulum placed on the PSA film with a magnetic force (Figure 3a). The logarithmic damping ratio of the material can be evaluated. The higher damping ratio of a material indicates the quick attenuation of the amplitude of the pendulum and the low modulus of the material. As shown in Figure 3b, Azo-M-0 has similar damping ratios (approximately 1.0) regardless

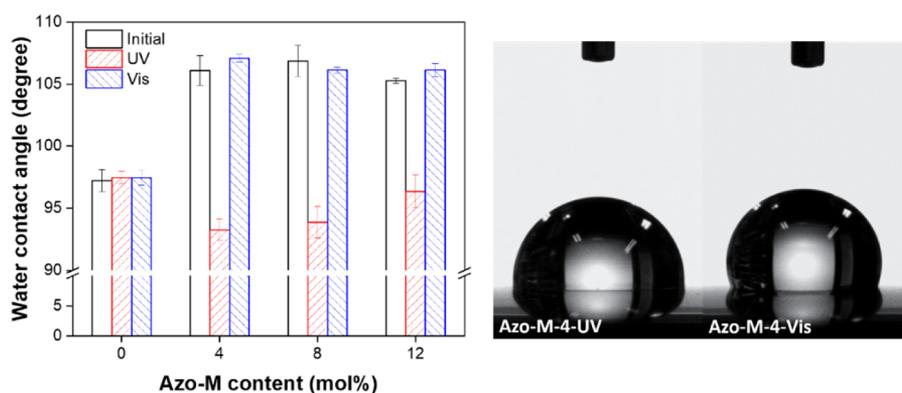


Figure 4. Transition of the water contact angle by UV and Vis irradiation.

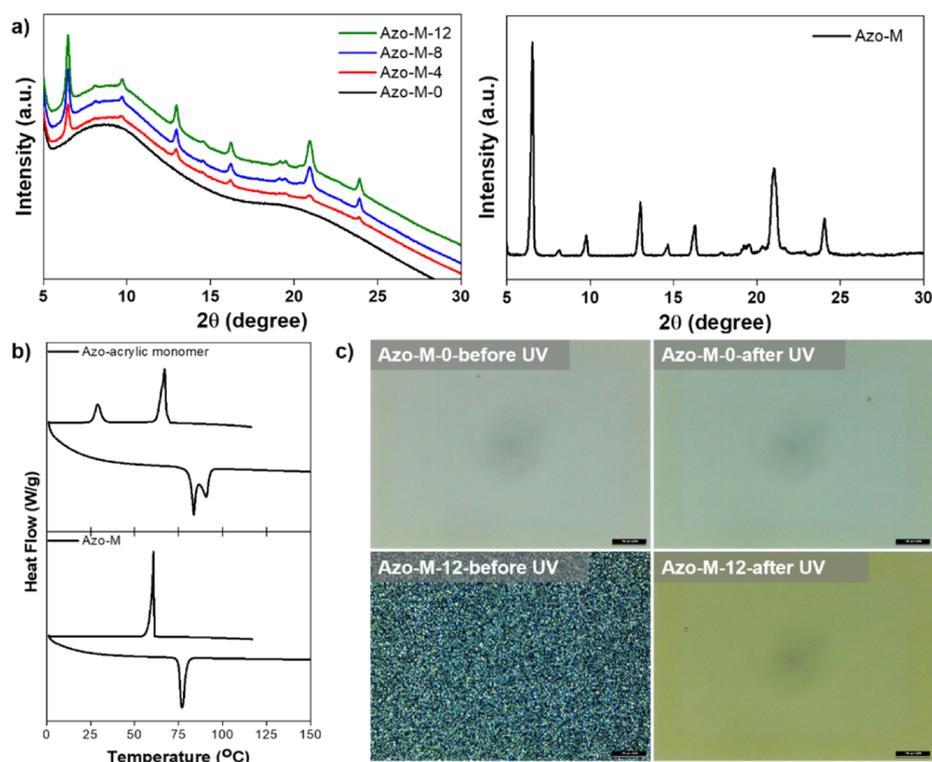


Figure 5. (a) XRD patterns of the switchable PSAs and Azo-M, (b) DSC profiles recorded for the azo-acrylic monomer and Azo-M, (c) POM images of Azo-M-0 and Azo-M-12 for observing the transition of crystalline structures under conditions of UV irradiation (X200).

of the irradiation conditions (UV or Vis irradiation). The damping ratios of the samples were observed to be the same as the damping ratio recorded for Azo-M-0 (i.e., approximately 1.0) when the Azo-M-4, 8, and 12 samples were irradiated with UV light. However, these values decreased when the azobenzene groups in Azo-M existed in their *trans*-form in the initial state and post Vis irradiation. The gap of the damping ratio (between the UV and Vis irradiation) increased with an increase in the Azo-M content (from 4 to 12 mol %). This result indicates that Azo-M-0 and other UV-irradiated samples dissipate energy rapidly. This can be attributed to their soft and sticky nature. The Vis-irradiated Azo-M-4, 8, and 12 samples became harder as the Azo-M content increases and the kinetic energy of the pendulum can be retained for a longer period of time.

We conducted a lap shear test using PMMA as a substrate to determine the shear modulus of the switchable PSA. Young's modulus and the shear modulus of the PMMA substrate are

approximately 3 and 2 GPa, respectively. The PMMA substrates were 150 times thicker than the sandwiched switchable PSAs. Thus, we assumed no interference from the PMMA substrate when measuring the shear modulus of the PSA. Further, we used DMA for precise testing. The stress-strain curves of the "switched on" switchable PSAs presented a very short or no linear region after UV irradiation (Figure S5). Therefore, we determined the shear modulus as the slope of the tangent line in the low-strain region below 2% (Figure 3c). The shear modulus of the UV-irradiated Azo-M-0 was 27 kPa, and this increased to 38 kPa in Azo-M-4. However, the modulus decreased with an increase in the Azo-M content. The addition of Azo-M introduces aromatic groups that result in a higher modulus (higher than that of the azo polymer). Azo-M was considered to play the role of a plasticizer with an increase in the content, owing to the disturbance in the arrangement of the monomers caused by *trans*-to-*cis* isomerization. The "switched off" switchable PSAs had a relatively long linear

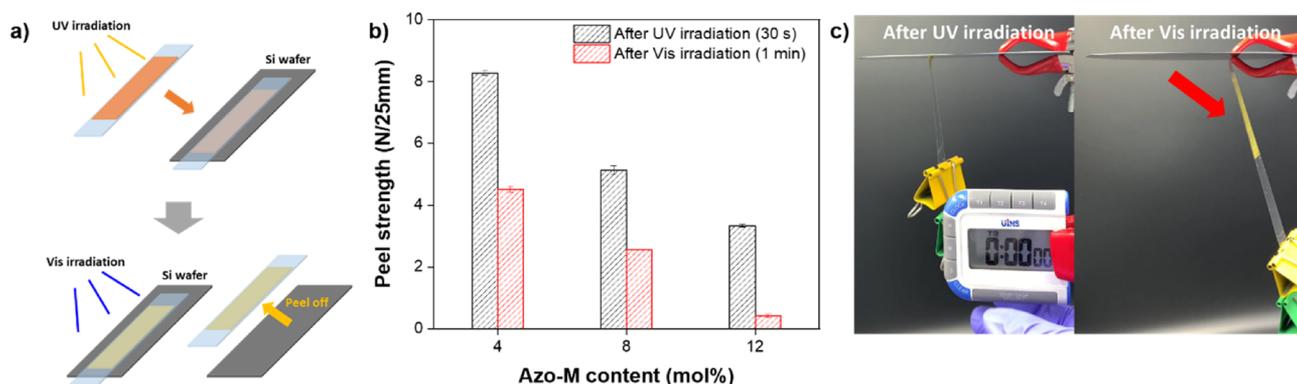


Figure 6. (a) Schematic representation of the peel strength switching evaluation method, (b) changes in the 180° peel strength of the switchable PSAs with UV and Vis irradiation, (c) images captured during the adhesion switching test by the 90° peel test conducted with Azo-M-12 (video, Supporting Information). The Vis-irradiated switchable PSA was peeled off immediately after the start of the test.

region in the stress–strain curves and a higher modulus than those of the “switched on” PSAs (except for Azo-M-0). The shear modulus increased with an increase in the Azo-M content. The modulus of Azo-M-12 was 78 kPa. Thus, the gap between the shear modulus of the “switched on” and “switched off” PSAs increased with an increase in Azo-M content.

The water contact angle was measured to observe the changes in the chemical characteristics of the PSA surface. The contact angle of Azo-M-0 was approximately 97° in the initial state and this value was maintained even after the samples were subjected to UV and Vis irradiation (Figure 4). When Azo-M was introduced, the contact angle became greater than 105° in the state where the azobenzene groups of the switchable PSAs existed in their *trans*-forms. The contact angle was lowered by *cis*-isomerization under conditions of UV irradiation. The contact angles of Azo-M-4, which exhibited the largest change in contact angle, were 107 and 93°. When the azobenzene moiety is isomerized (from *trans* to *cis*), it loses its symmetric structure. The dipole moment of the *cis*-isomer is higher than that of the *trans*-isomer. Therefore, the polar *cis*-azobenzene increased the surface energy of the PSA sample after UV irradiation, as shown by the decrease in the water contact angle.⁴⁸ Meanwhile, a low surface energy was observed for *trans*-azobenzene. This can be attributed to the crystalline structure formed by π - π stacking between the azobenzene groups.⁴⁹ The switching gap of the contact angles decreased as the content of Azo-M increased, but the change was insignificant (within 3°).

In the “switched off” state, the modulus and hydrophobicity increased when Azo-M was added to the azo polymer. The probe tack decreased to almost zero. According to eq 2, an increase in the modulus induces an increase in the adhesive force. A zero tack value could not be explained in terms of hydrophobicity because the correlation assumes an equilibrium state where the probe and adhesive have completely adhered. A wetting process is necessary to achieve adhesion between the PSA and the substrate, and wettability depends on surface energy and the modulus.⁴ Unlike the wettability of liquid (which is determined by analyzing the surface energy), that of the PSA is restricted by the modulus. Therefore, the restriction of the wettability of the PSA caused by the higher hydrophobicity and modulus induced the formation of the nonsticky surface and the “switched off” property. The decrease in the hydrophobicity and modulus (attributable to UV irradiation) made the switchable PSA sticky and wettable.

The probe tack was unrelated to the Azo-M content despite the bigger modulus gap between the “switched on” and “switched off” states of the PSAs. It can be inferred from the results that 4 mol % of Azo-M is sufficient to switch off the probe tack. The differences in shear modulus cannot affect the probe tack results.

The XRD patterns of the switchable PSAs were recorded. The gentle slope in a wide range of 2θ in the XRD pattern indicates that the azo polymer was amorphous (Figure 5a). As Azo-M was added, peaks were observed at 6.5, 9.6, 12.9, 16.2, 21.1, and 23.9°. The patterns showed that Azo-M formed its own crystalline structure in the switchable PSA, because the crystalline patterns of the switchable PSAs matched the pattern recorded for Azo-M. We confirmed that the azo-acrylic monomer used to polymerize the azo polymer had crystallinity using the DSC (Figure 5b). It also had a mesophase, which is a characteristic of liquid crystals between 29 and 67 °C, as shown during the cooling scan of the DSC measurement. However, the azo-acrylic monomers present in the polymer chain could not form a crystalline structure or mesophase in the PSA as their content was low (8 mol %) and due to the interference from the co-monomer (BA).

Further, we observed small and dense crystalline structures (formed in the switchable PSA) using POM (Figure 5c and Figure S6). No crystalline structure was observed in the absence of Azo-M (as indicated by the XRD results). The crystalline structure disappeared in the POM image of the switchable PSA under conditions of UV irradiation. The *trans*-azobenzene has a planar structure and can be stacked easily, whereas the three-dimensionally distorted structure of the *cis*-azobenzene disturbs the molecular arrangement. This transition in crystalline structure is expected to induce changes in hydrophilicity and the modulus that enable adhesion switching.

We attempted to convert the azo polymer to poly(butyl acrylate) (PBA) to define the function of the azo polymer in the switchable PSA. The Azo-M contents were set to 12, 16, and 20 (mol %), considering that 8 mol % of the azobenzene moiety was present in the azo polymer. However, a nonuniformly stained film was obtained (Figure S7a). When we tested the switchable probe tack, marks were left on the surface of the PSA and residue was left on the probe (Figure S7b). We confirmed that Azo-M could be stably dispersed and fixed in the switchable PSA by making it interact with the azobenzene moiety in the azo polymer.

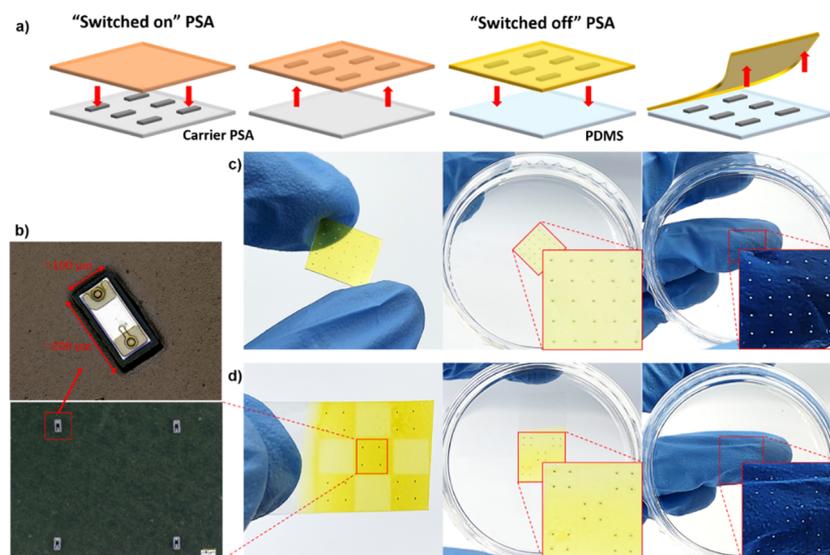


Figure 7. (a) Schematic representation of the mini-LED transfer test method using switchable PSAs (donor: carrier PSA, acceptor: PDMS), (b) confocal and optical microscopy images of mini-LEDs, (c) the mini-LED transfer test using Azo-M-12, (d) selective transfer by the partial adhesion switching of Azo-M-12 using a photomask.

We conducted a 180° peel test to evaluate the property of adhesion switchability even in the adhered state to the substrate (Figure 6a). The peel strength of the “switched on” Azo-M-4 was the highest, and it tended to decrease as the Azo-M content increased (Figure 6b). All samples showed a reduction in adhesion when irradiated with Vis light. The switching ratio ($F_{\text{high}}/F_{\text{low}}$, where F_{high} denotes the peel strength of the “switched on” PSA and F_{low} denotes the peel strength of the “switched off” PSA) increased with a decrease in F_{high} . Contrary to the probe tack results, which suggested that the Azo-M content and adhesion were not related, the peel test showed that as the Azo-M content increased, the adhesion forces of the “switched on” PSA decreased and the switching ratio increased. Thus, the surface property had a more dominant influence on the probe tack, whereas the modulus significantly influenced the peel strength. The peel test confirmed that the switching characteristic was achieved even when the switchable PSA was attached to the substrate. Thus, we believed it could be used as a mediator in the transfer process.

We investigated if the switchable PSA can be used to transfer mini-LEDs. The mini-LEDs were arrayed on the carrier PSA. The width and length of the mini-LED were 100 and 200 μm , respectively. We transferred the mini-LEDs from the carrier PSA as the donor to PDMS as the acceptor. The adhesion forces evaluated by the probe tack test of the donor and acceptor were approximately 40 and 70 kPa, respectively (Figure S8). The transfer process is shown in Figure 7. We conducted the experiments with Azo-M-12 because it exhibited the maximum switching ratio. The mini-LEDs were picked up by the UV-irradiated switchable PSA, and the mini-LEDs were transferred to the switchable PSA successfully. The switchable PSA was placed onto the PDMS and then peeled off post Vis irradiation. The mini-LEDs were successfully transferred onto the PDMS. Further, we examined the property of selective transfer by local UV irradiation using a photomask. The UV-irradiated parts appeared dark yellow. It was confirmed that only the mini-LEDs located under the UV-irradiated parts were transferred to the switchable PSAs.

4. CONCLUSIONS

We prepared switchable PSAs using a mixture of an azo polymer and Azo-M. The azo polymer allowed Azo-M to be uniformly and stably dispersed in the PSA. The modulus and surface energy were tuned with UV and Vis irradiation. The change in the properties can be attributed to the crystalline structure transition exhibited by Azo-M (via photoisomerization). The switchable PSAs exhibited the property of fast adhesion switching and a high switching ratio without phase transition between the solid and liquid states. Repetitive adhesion switching without a loss in adhesion force was also achieved. The novel switchable PSA can be potentially used as a selective and reusable transfer film for microscaled electronic devices. They can be used to realize mini-LED and micro-LED transfer processes. The study was limited to the synthesis and characterization of a polymer and monomer with specific structures and the preliminary test of mini-LED transfer. The effects of various monomers (differing in their chemical structures) are under investigation. Mass transfer processes are also being researched.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c11680>.

¹H NMR spectra for all compounds, shear stress–strain curves and POM images for all specimens, photographs and adhesive forces for the switchable PSAs using PBA, and adhesive forces for the donor and acceptor of mini-LED transfer test (PDF)

Adhesion switching test (MP4)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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