



A DISSERTATION FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Photocatalyst-mediated Visible Light Curable Acrylic Pressure Sensitive Adhesive for Mobile Display

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Abstract

Photocatalyst-mediated Visible Light Curable Acrylic Pressure Sensitive Adhesive for Mobile Display

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Pressure sensitive adhesive (PSA) is a polymeric material used to adhere to various substrates by light pressure. PSAs are classified into rubber-based, polyacrylate-based, and silicon-based PSA according to their chemical compositions. Acrylic PSA has been widely used thanks to its excellent properties, including oxidant resistance, optical transparency, yellowing-free, and high adhesive strength. Based on its excellent properties, acrylic PSA has become an essential material for assembling mobile displays, and the requirements for the PSA are different for each layer. For instance, the PSA on the top of the emitting layer requires transparency (optically clear adhesive, OCA). In contrast, the PSA for release film and back film/plate requires low and high adhesive strength, respectively.

One of the essential advantages of acrylic PSA is its light-curable ability because light curing enables fast curing, cost reduction, and solvent exclusion. Although light-curable acrylic PSA has been manufactured mainly using a UVactive photoinitiator (PI), visible light-curing has significant advantages over UV-curing (light-curing ability under UV-blocking conditions). Herein, we newly developed light-curable acrylic PSAs for mobile displays, and a visiblelight-active photocatalyst was employed to initiate polymerization under visible light conditions. Although the amount required for polymerization is much less for photocatalyst than PI, the content of photocatalyst absorbing visible light needs to be reduced further to produce transparent PSA for mobile displays. Thus, the efficiency of the photocatalyst should be improved to maintain the curing rate even at low photocatalyst loadings. This study used three strategies to improve photocatalyst's efficiency; driving the catalytic cycle by 1) typical monomers used for acrylic PSAs or 2) additives. 3) Optimizing the catalytic cycle using various photocatalyst s and additives. After improving the photocatalyst's efficiency, we designed the acrylic PSAs for mobile displays, considering many factors; glass transition temperature, viscoelastic properties, degree of crosslinking, adhesive performances, and minimized additives.

First, we employed a typical monomer to drive the catalytic cycle of the photocatalyst. *N*-vinyl-based monomer is a typical monomer for acrylic PSAs, improving the cohesive strength. In addition, it acts as a reducing agent to drive the reductive quenching cycle of the excited photocatalyst. Next, we used 4DP-IPN as photocatalyst because of its excellent catalytic performance (triplet generation, strong visible light absorption, high photo/electrochemical stability, and proper redox potentials). Then, visible-light-curable PSAs were prepared in two steps (bulk polymerization and film curing). *N*-vinyl-based monomer greatly enhanced the polymerization rate, and the mechanism of the initiation by *N*-vinyl-based monomer was proposed. We next manufactured various visible-light-curable PSAs with different monomer compositions and confirmed that their properties (viscoelasticity, physical properties, and adhesive performances) could be adjusted in a wide range. Notably, despite the poor transparency of the prepared visible-light-curable PSA due to high

photocatalyst loading (50 ppm), their adhesive performances were widely adjusted. Thus, the prepared PSAs were expected to be utilized for release film (requires low adhesive strength) or back film/plate (requires high adhesive strength) in mobile displays.

Second, the catalytic cycle of 4DP-IPN was driven by additives (α -haloester) to prepare the OCA for mobile displays. α -haloester is an oxidant known to facilitate the oxidative quenching cycle of 4DP-IPN. Three α -haloesters were employed, and we confirmed the best oxidant (diethyl 2-bromo-2-methylmalonate, DBM) to drive the catalytic cycle of 4DP-IPN. The prepared visible-light-curable acrylic PSA with the optimal composition (10 ppm of 4DP-IPN and 0.1 mol% of DBM) exhibited excellent adhesive performances and a fast polymerization rate. In particular, the prepared PSAs showed excellent transparency (approximately 100% at 400 nm) with decreasing 4DP-IPN content to 10 ppm. Therefore, the prepared visible-light-curable PSAs were expected to be utilized for OCA in mobile displays.

Third, the catalytic cycle was optimized to produce UV-blocking OCA by visible light-curing. Various photocatalysts and reductants with different the highest occupied molecular orbital levels were used, and we found the optimal combination of them (10 ppm of 4Cz-IPN and 0.5 mo% of 2-(dimethylamino)ethyl acetate; DMAEAc). Next, we used another reductant (2-(dimethylamino)ethyl acrylate; DMAEA) structurally similar to DMAEAc but induced crosslinking. Two reductants (DMAEAc and DMAEA) were used simultaneously as the hybrid reductant to fine-tune the crosslinking degree of OCAs for foldable displays. We found the optimal ratio of the hybrid reductant (40% or 60% of DMAEA) exhibiting suitable properties (gel content, peel strength, strain recovery, and stress relaxation) for foldable displays. At last, we manufactured the UV-blocking OCAs by incorporating the optimal content of

UV absorbers. It was demonstrated that visible light-curing was considerably more efficient than traditional UV-curing for fabricating UV-blocking OCAs. Furthermore, the produced UV-blocking OCAs exhibited excellent performances (transparency, UV protection, adhesive performances, and viscoelastic properties) that could be used for foldable displays. In addition, it is important to note that the folding stability of the prepared UV-blocking OCA was excellent under various testing conditions ($25 \,^{\circ}$ C, $-20 \,^{\circ}$ C, and $60 \,^{\circ}$ C/93%). Conclusively, the produced visible-light-curable UV-blocking OCA showed high potential to be utilized in foldable displays.

Keywords: Photocatalyst, Visible Light Curing, Acrylic Pressure Sensitive Adhesive (PSA), Optically Clear Adhesive (OCA), UV-Blocking OCA, Mobile display

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Introduction

1. Introduction

1.1. Acrylic Pressure Sensitive Adhesives

1.1.1. Basic Properties

Pressure sensitive adhesive (PSA) is a polymeric material that is permanently sticky in dry form and firmly adheres to various adherents (Creton, 2003). PSA differs from solvent/thermal activatable adhesives and hot melt adhesives because it exhibits tackiness in solvent-free dry form at room temperature. Since the first large-scale production of PSA in 1874 by Robert Wood Johnson, who is the founder of the global company (Johnson & Johnson) (Satas, 1999), its usage has been widely extended from medical tapes (Dickson, 1926) to electrical tapes (Frank, et al., 1935), masking tapes (Drew, 1933), labels (Avery, 1940), packaging tapes (Michael, 1938), protective films (James, 1952), and others. The world's first PSA was produced using natural rubber in 1859 (Day, 1859), and rubber-based PSA was traditionally composed of natural rubber and tackifying resin. At the beginning of World War II, the United States struggled with the supply of natural rubber, and thus the research to substitute natural rubber with synthetic rubber was prompted. Accordingly, synthetic rubber was used to produce rubber-based PSA, which is widely used nowadays. However, rubber-based PSA is currently limited in medical products because it causes skin irritation. Rubber-based PSA should contain the tackifying resin that grants tackiness to the PSA and causes skin irritation. All of the early medical PSAs used the rubber-based PSA, which caused skin irritation problems. To address this issue, in the 1960s, acrylic PSA, excluding the tackifying resin, emerged as a substituent for the rubber-based PSA.



Figure 1-1. Classification of monomers used for acrylic PSAs (Satas, 1999).

Acrylic PSA has several advantages: inherent tackiness without low molecular weight resin, transparency, high adhesive strength, oxidation resistance, etc (Tobing, et al., 2001). Thanks to those advantages, acrylic PSA has been considered the most useful PSA. As shown in Figure 1-1, acrylic PSA is generally composed of three types of acrylic monomers: main monomers (50~98%), modifying monomers (10~40%), and monomers with functional groups (0.5~20%) (Satas, 1999). For PSA to become rubbery at room temperature, glass transition temperature (T_g) should be sufficiently low, and main monomers with low T_g are essential to achieve this. Because homopolymers of main monomers are too soft to be used as PSA, modifying monomers with higher T_g than main monomers are used to precisely control the $T_{\rm g}$ of PSA. To further improve the performance of acrylic PSA, monomers with functional groups are copolymerized. Various functional groups (carboxylic acid, hydroxy, epoxide, and isocyanate) facilitate inter- or intramolecular noncovalent bondings. These bondings improve the cohesive strength and interfacial adhesion. Furthermore, the cohesive strength and thermal stability of acrylic PSA are further improved by the reaction between functional groups, which induces a crosslinking network (Tobing, et al., 2001).

1.1.2. Preparation of Acrylic Pressure Sensitive Adhesive

Polyacrylate for PSA has been usually produced by radical-mediated polymerizations (Figure 1-2) (Ballard, et al., 2018): bulk polymerization, solvent-based polymerization, and emulsion polymerization. Bulk polymerization is the simplest polymerization that uses monomers and initiators. Bulk polymerization has severe problems with thermal management because monomers are consumed during the polymerization, and viscosity exponentially increases. Solvent-based polymerization addresses this issue by using organic solvent-dissolving monomers and polymers. Because of the stringent regulations using organic solvents, emulsion polymerization that uses water instead of organic solvents emerged. All polymerizations above have been conventionally initiated by a thermal initiator that generates radicals at elevated temperatures. However, photoinitiator generating radicals by exposure to light facilitates extremely fast polymerization without elevating temperature (Decker, 1996).



Figure 1-2. Radical polymerization of acrylate monomers (Ballard and Asua, 2018).

1.1.3. Pressure Sensitive Adhesive for Mobile Displays

Based on their excellent performances, acrylic PSAs have been applied to many industries, including mobile displays. In particular, many PSAs are essentially used for assembling mobile displays (**Figure 1-3**), and different physical properties are required for each PSAs. For example, the PSA (precisely optically clear adhesive, OCA) on the top of the OLED panel requires excellent transparency. In addition, the PSA for the back film (or back plate) requires high adhesive strength, whereas the PSA for the protection film or the release film exhibits low adhesive strength to be well detached. Therefore, when designing adhesives for displays, transparency and adhesive strength must be considered first, and other properties (haze, yellow index, reliability to light/heat/humidity) are additionally evaluated for commercial product production. In particular, all PSAs (except for PSA in the back plate) should exhibit excellent folding stability for a foldable display.



Figure 1-3. Example of the mobile display structure: expected structure of "Galaxy Z Fold3" (Yi, *et al.*, 2021).

1.2. Photopolymerization

1.2.1. Photopolymerization by Photoinitiator

Photoinitiator (PI) is the most common substance to initiate photopolymerization and generates radicals in two ways (**Figure 1-4**). In Norrish type 1 reaction, light induces homolytic cleavage of PI, and two radicals are generated from a single molecule. Hydrogen abstraction from hydrogen donor (R-H) to excited PI (PI=O*) generates radicals (•PI-OH and R•) by Norrish type 2 reaction, and the generated radicals initiate polymerization to produce polyacrylate.





Figure 1-4. Radical generation mechanism of PI (Decker, 1996).

Photopolymerization with UV-active PI is mainly used to manufacture radiation-curable PSA, and there are many types of PI (**Figure 1-5**): benzoin derivatives, hydroxyalkylphenones, α -amino ketones, acylphosphine oxides, benzophenone derivatives, and thioxanthone derivatives (Decker, 1996). Therefore, it is essential to select the proper PI among many candidates. Many factors should be considered, *e.g.*, compatibility and initiation efficiency, and the selection of light wavelength is one of the most important things. For example, benzophenone absorbs light at the wavelength of 253 nm, while diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) absorbs light at a higher wavelength (295, 368, 380, and 393 nm). It presents that TPO is more suitable than benzophenone to generate radicals when a light source with a higher wavelength is used. On the other hand, visible-light-active PI, such as Irgacure 784, has an advantage that can generate radicals with a higher wavelength than 400 nm. However, it causes severe problems such as metal contamination.



Irgacure 784

Visible light-active photoinitiator



Figure 1-5. Examples of visible light-active or UV-active PI (Decker, 1996).

Czech and coworkers have extensively investigated various PIs for the production of light-curable PSAs (**Figure 1-6**) (Czech, 2007, Czech, *et al.*, 2011, Czech, *et al.*, 2012, Czech, *et al.*, 2013, Czech, *et al.*, 2021). They confirmed that both Norrish type 1 and 2 PIs could be used to manufacture acrylic PSAs. Norrish type 1 PI generates radicals by homolytic cleavage of PI itself, but Norrish type 2 PI abstracts hydrogen from acrylate to generate radicals. Additionally, they found that PI containing vinyl group can be copolymerized; thus, PI acts as both initiator and monomer.

Visible light-active PI can also be used in the medical industry, and commercial products of visible light-switchable PSAs are already released (Figure 1-7) (AB, 2022). The origin of the visible light-switchable PSAs was studied by Webster and coworkers (Boyne, et al., 2001, Webster, 1999). They discovered that the highly crosslinked network of PSAs leads to low peel strength facilitating easy removal from the skin. Acrylic polymers were firstly prepared by thermally initiated FRP of acrylate monomers and itaconic anhydride to prepare visible light switchable PSAs (Figure 1-8). Next, the linear polymer containing the methacrylate group on the side of the chain was prepared by a ring-opening reaction of anhydride. The linear polymer-based PSA showed sufficiently high peel strength; thus, the PSA could be firmly attached to the skin. However, when visible light-active PI was added to the linear polymer resin, the linear polymer was transformed into a crosslinked network by exposure to visible light. The peel strength of PSA generally decreased with increasing its crosslinking density; thus, the crosslinked network-based PSA showed low peel strength. However, a large amount of visible light-active PI (5~10 wt%) was required, which could deteriorate the transparency of the prepared PSA.



Figure 1-6. Various PIs for light curable acrylic PSAs (Czech, 2007, Czech, et al., 2011, Czech, et al., 2011, Czech, et al., 2012, Czech, et al., 2013, Czech, et al., 2021).



Figure 1-7. Examples of visible light-curable PSA in medical tapes (AB, 2022).



Figure 1-8. Light switchable PSA using visible light active PI (Boyne, *et al.*, 2001, Webster, 1999).
1.2.2. Photopolymerization by Photocatalyst

Photosensitization and photoredox catalysis are promising techniques that can address the issue of visible-light-active PI by excluding inorganic materials. Although these two processes look very similar, they are usually distinguished by whether they involve energy transfer. Photosensitization usually involves energy transfer, whereas photoredox catalysis involves electron or hydrogen transfer (Michelin, *et al.*, 2018). Additional substances that generate reactive species should be incorporated to initiate photopolymerization via photosensitizer or photocatalyst. For example, camphorquinone, a kind of photosensitizer (or photocatalyst), should be used with a hydrogen donor (sometimes called a co-initiator) to initiate photopolymerization (**Figure 1-9**).



Figure 1-9. Example of generating reactive species using camphorquinone (Schroeder, *et al.*, 2013, Shi, *et al.*, 2017).

One of the essential advantages of the photocatalyst is its regeneration characteristic. For example, **Figure 1-9** shows that ground-state CQ can be regenerated from hydrogenated camphorquinone (CQ-H•) using a sacrificial hydrogen acceptor (Ph₂I⁺X⁻). Regeneration characteristics can significantly reduce photocatalyst loading to ppm level (Dadashi-Silab, *et al.*, 2016), and it is essential to note that the reduction of photocatalyst amount improves the transparency of the final products.

In order to lower the input amount of the photocatalyst, the regeneration process of the photocatalyst should be accelerated. For this purpose, an understanding of the catalytic cycle of photocatalyst is required. The catalytic cycle of photocatalyst is composed of three parts (Figure 1-10): i) excitation of photocatalyst by absorbing light, ii) quenching of the excited photocatalyst (photocatalyst*) via photoinduced electron transfer, and iii) regeneration of ground state photocatalyst. The excited photocatalyst (photocatalyst*) can be quenched by oxidative or reductive quenching. In the oxidative quenching cycle, photocatalyst* is quenched by an electron acceptor (EA), and the quenched photocatalyst radical cation (PC++) is transformed to ground state photocatalyst by an electron donor (ED). Conversely, photocatalyst radical anion (PC•–) is generated by ED-induced reductive quenching, and then ground state photocatalyst is regenerated by accepting an electron from EA. Additives that donate or accept an electron are essential to driving the quenching cycle of photocatalyst, and the effectiveness of electron transfer between photocatalyst and additives determines catalytic performances of photocatalyst (vide infra for detail).



Figure 1-10. Oxidative quenching cycle and reductive quenching cycle of photocatalyst. PC, EA, and ED mean photocatalyst, electron acceptor, and electron donor, respectively.

For a comprehensive understanding of electron transfer of the excited photocatalyst, photophysical processes and redox potentials should be described (Figure 1-11) (Romero, et al., 2016). Photocatalyst absorbs light (hv) to generate the excited photocatalyst (PC*), and an electron generally is excited from a ground state singlet (S_0) to a singlet excited state. An electron can be excited to singlet excited states on different vibrational energy levels, but it is quickly relaxed to the lowest energy level (S_1) within picoseconds. The excited photocatalyst loses its energy in radiative (emitting light) or nonradiative ways (energy dissipation by heat): the excited singlet (S_1) returns to S_0 by a radiative transition (fluorescence) or a nonradiative transition (inter conversion, IC). When the photocatalyst absorbs light, the excited singlet (S_1) and the excited triplet (T_1) are generated, and S_1 can be transformed to T_1 by a nonradiative process (intersystem crossing, ISC). The quantum yield of ISC (φ_{ISC}) should be enlarged to improve catalytic performances (see below for a reason). In the excited state of photocatalyst, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) contain one electron each. Therefore electron-donating ability (donating a single electron in LUMO) and electron-accepting ability (accepting an electron to a single vacancy in HOMO) are excellent for the excited photocatalyst. For this reason, the excited photocatalyst can be easily quenched via photo-induced electron transfer: in reductive or oxidative ways. For effective oxidative quenching of photocatalyst, $E_{ox}^{*}(PC^{+}/PC^{*})$ should be lower than 0, and conversely, $E_{red}^*(PC^*/PC^{\bullet})$ should be higher than 0 to drive reductive quenching. It is highly required to restrict the back electron transfer (BET) that causes recombination between photocatalyst/additives radical ion pairs to increase the efficiency of photo-induced electron transfer.



Figure 1-11. Photophysical processes and ground state/excited state redox potentials of photocatalyst (Romero and Nicewicz, 2016).

The excited triplet (T_1) shows a sufficient lifetime and less probability for BET; thus, the high population of T_1 ensures efficient photo-induced electron transfer. However, T₁ should be generated by ISC from S₁, and a transition in which spin multiplicity is changed is a forbidden process. The rate of ISC strictly depends on i) the energy gap between S1 and T1 and ii) spin-orbit coupling (SOC). The orbital motion induces a change in the spin motion of an electron, and this interaction is called SOC. The spin motion is greatly affected by an internal/external heavy atom with a large nucleus: a heavy atom effect. Based on the El-Sayed rules, the orthogonal transition $({}^{1}n,\pi^{*}\rightarrow{}^{3}\pi,\pi^{*})$ or ${}^{1}\pi,\pi^{*}\rightarrow{}^{3}n,\pi^{*})$ shows much higher SOC than localized transition $({}^{1}n,\pi^{*}\rightarrow{}^{3}n,\pi^{*})$ or ${}^{1}\pi,\pi^* \rightarrow {}^{3}\pi,\pi^*$). In summary, the best photocatalyst for effective photoinduced electron transfer should exhibit a high population of T_1 , which can be achieved by employing a heavy atom, facilitating orthogonal transition, or reducing the energy gap between S_1 and T_1 . The polypyridyl complex of ruthenium (Ru(bpy) $_{3}^{2+}$) is a representative transition metal-based photocatalyst with a high population of T_1 , induced by a heavy atom effect. Ru(bpy)₃²⁺ has several advantages (strong absorption at 452 nm, long-lived excited state, and effective excited state oxidant/reductant) to be used as visible light active photocatalyst (Prier, et al., 2013). However, organic photocatalysts have been extensively developed for metal-free organic reactions (Figure 1-12) (Romero and Nicewicz, 2016). The halogen-based organic photocatalysts show high SOC thanks to the heavy atom effect. photocatalysts with strongly twisted donor-acceptor structures exhibit a small energy gap between S₁ and T₁ that facilitates ISC from S_1 to T_1 .



Figure 1-12. Common organic photocatalysts (Romero and Nicewicz, 2016).

Photopolymerization shows excellent polymerization behavior without solvent or heating; thus, it has grown mainly over the last half-century (Decker, 1996). However, radical-induced photopolymerization is vulnerable to inhibition by oxygen molecules, which is called oxygen inhibition. Photopolymerization should be conducted after degassing or conducted under conditions isolated from external air to avoid oxygen inhibition (Ligon, *et al.*,

2014). These conditions generally increase production costs and strictly confine the application range of photopolymerization. For example, light-induced bulk polymerization of acrylate monomers should be conducted after the degassing process. It takes longer to purge inert gas with increasing production scale, which causes an increase in production costs.

Oxygen tolerance of photopolymerization can be achieved by generating active radical species from inactive radical species (Figure 1-13) (Ligon, et al., 2014). Oxygen molecules react with propagating radicals, and peroxyl radicals (POO•) are generated, an inactive radical species that cannot initiate acrylate polymerization. These peroxyl radicals undergo radical combination or hydrogen abstraction, generating inactive species (POOP, POOH, R•). Hydrogen donors (DH) and reducing agents (RA) are generally employed to transform inactive radical species into active ones. Hydrogen abstraction at hydrogen donors generates active radical species (D•), and chain transfer by reducing agents generates PO• that can reinitiate acrylate polymerization. Another strategy to grant oxygen tolerance is to generate reactive radicals (PO• or HO•) by decomposing the POOP and POOH. In addition to chemical approaches to convert inactive radical species to active radical species, physical approaches such as higher light intensity also reduce oxygen inhibition. A photocatalyst-mediated photopolymerization is a powerful tool for granting oxygen tolerance. Oxygen in a monomer mixture facilitated radical generation via photocatalyst's oxygen-mediated reductive quenching pathway (Wu, et al., 2021).



Figure 1-13. Strategies to reduce oxygen inhibition in photopolymerization (Ligon, *et al.*, 2014).

1.3. Application of Photocatalyst-mediated Photopolymerization

1.3.1. Hydrogel

Photocatalyst-mediated photopolymerization has been widely used for many applications: coatings, dental resins, drug delivery, hydrogels, light-driven 3D printing materials, and adhesives (Dadashi-Silab, *et al.*, 2016). For example, a biocompatible photocatalyst with water solubility and oxygen tolerance is essential for preparing light-curable hydrogel. Eosin Y is one of the most valuable photocatalysts for fabricating hydrogels by gently irradiating visible light under atmospheric conditions (Avens, *et al.*, 2009, Kuck, *et al.*, 2008, Sawhney, *et al.*, 1993). *Sikes* group investigated the origin of oxygen tolerant catalytic cycle of eosin Y-mediated photopolymerization using *N*-vinylpyrrolidone. They proposed a plausible mechanism for an oxygen-mediated photocatalytic cycle, as shown in **Figure 1-14** (Aguirre-Soto, *et al.*, 2019). In this reference, only a small amount (~ 7 ppm) of eosin Y was employed to polymerize hydrogel, but a long curing time (> 15 min) was required.



Figure 1-14. Eosin Y-mediated photopolymerization mechanism (Aguirre-Soto, *et al.*, 2019).

1.3.2. Light-Driven 3D printing

In addition to hydrogel, photocatalyst-mediated photopolymerization has been widely used in light-driven 3D printing techniques. Page and coworkers extensively investigated visible-light-driven 3D printing (Ahn, et al., 2020, Ahn, et al., 2021, Stevens, et al., 2022). They developed an efficient photocatalytic system to facilitate excellent performance in light-driven 3D printing. In lightdriven 3D printing, visible-light-curing has many benefits over UV-curing: biocompatibility, functional group tolerance, superior penetration depth, and reduced scattering. However, the curing rate and resolution are restricted when using visible-light-curing than UV-curing. They studied efficient visible-lightcuring with various wavelengths (blue, green, and red), facilitating rapid builds and high resolution using photocatalyst, opaquing agent, and electron donor/acceptor (Ahn, et al., 2020). H-Nu-470, Rose Bengal, and Zn-TPP are visible light-active photocatalyst that absorbs blue (460 nm), green (525 nm), and red (615 nm), respectively. Iodonium/borate is used as an electron acceptor/donor, and BAPO is violet-active PI used in conventional light-driven 3D printing. They found that electron acceptor oxidatively quenches photocatalysts, and ground state photocatalysts are regenerated by an electron donor (Figure 1-15 a and b). This photocatalytic cycle achieved a rapid curing rate (33 ~ 45 mm/h) for three different visible-light-curing (blue/green/red). In addition to the curing rate, a high resolution was obtained using an opaquing agent (azo-dyes) that absorbed light to reduce the penetration depth and prevent curing in the unwanted region (Figure 1-15 c and d). However, this study had minor disadvantages; they used a metallic compound as a red light-active photocatalyst (Zn-TPP), and the photocatalyst content was relatively high (0.1 ~ 0.3 wt%).



Figure 1-15. a) Photo-induced FRP for 3D printing using various photocatalyst; b) electron acceptor (A), electron donor (D), and c) opaquing agent (OA). d) light absorption of PI and OA (Ahn, *et al.*, 2020).

Page and coworkers next investigated a strategy to reduce oxygen inhibition in light-driven 3D printing (Ahn, et al., 2021). Thiol-based multifunctional additive (PETMP) was used to facilitate photopolymerization under air conditions (Figure 1-16 a). Oxygen was consumed in two ways: i) hydrogen abstraction of S-H by peroxy radical (Figure 1-16 b) and ii) reductive quenching pathway of ZnTPP (Figure 1-16 c). First, peroxy radical is formed by a reaction between oxygen molecules and propagating radicals, and peroxy radical cannot react with acrylate monomers but can abstract the hydrogen of PETMP. By hydrogen abstraction, S radical is generated, and this radical reacts with acrylate monomers, and thus free radical polymerization is still being proceeded even under oxygen conditions. This mechanism can be applied to both PI-induced and photocatalyst-induced FRP, such that BAPO-derived FRP also showed oxygen tolerance when using PETMP. Second, in the reductive quenching pathway of photocatalyst, the excited photocatalyst interacts with triplet state oxygen $({}^{3}O_{2})$ or thiol (S-H), and singlet state oxygen $({}^{1}O_{2})$ or thiol radical cation is generated. The generated thiol radical cation is oxidized, and the generated thiol radical undergoes an anti-Markovnikov thiol-ene addition with acrylate. The resulting sulfides might react with ¹O₂, and sulfoxide is formed. A resin containing photocatalyst and thiol can be cured under air conditions via the mechanism above. They confirmed that the induction period sharply decreased from 49.4 s to 5.8 s with the addition of 1 wt% of PETMP, which shows significantly improved oxygen tolerance (Figure 1-16d). Direct reaction of thiol with acrylic polymer network also reduces unfavorable odors and leaching of additives. They used a large amount of photocatalyst (0.3 wt%), but it was not a big deal because transparency is unnecessary for 3D printing (Figure 1-16e). However, it would have been better to use an organic photocatalyst rather than a metal-based catalyst.



Figure 1-16. a) Strategy to reduce oxygen inhibition in light-driven 3D printing. Proposed mechanism for oxygen tolerance induced by b) thiol and c) reductive quenching cycle (Ahn, *et al.*, 2021).

The other group, Boyer and coworkers, also investigated light-driven 3D printing (Bagheri, et al., 2021, Zhang, et al., 2021). They employed photoinduced electron transfer-induced living/controlled radical polymerization rather than FRP because of the homogeneity of the final products. FRP generates nanogels incorporating highly crosslinked networks because of rapid chain growth and termination. On the other hand, living/controlled radical polymerization, such as reversible addition-fragmentation chain transfer (RAFT), induces more homogeneous polymer networks thanks to the controlled polymerization rate (Figure 1-17a). Previously, RAFT agents for 3D printing were strictly limited to trithiocarbonate-type agents, and they studied various RAFT agents with different activating groups (Z) and leaving groups (R) (Figure 1-17b). Polymerization kinetics were analyzed with the RAFT agents' stability, fragmentation efficiency, and radical stabilization energy. It was found that the curing rate was lowered by adding RAFT agents, and specific RAFT agents (CDTPA, DBTTC, DTC2) significantly deteriorated the curing rate. They also investigated RAFT agents' effect on the final product's physical properties (Figure 1-7c). Because of the more crosslinked polymer networks, storage modulus (E') and glass transition temperature (T_g) increased with increasing curing time. As RAFT agents were incorporated into the resin formulations, E' and $T_{\rm g}$ decreased because of fewer crosslinked networks. However, under a specific RAFT agent condition (BTPA, 50 equiv.), E' at glassy state was higher than the control specimen (no RAFT agent). It might result from less generation of nanogels by RAFT, which resulted in reduced free volume. They showed that the photo-induced electron transfer-RAFT system with photocatalyst and BTPA exhibited excellent curing behavior and physical properties, but a relatively large amount of photocatalyst (~100 ppm) was employed.



Figure 1-17. a) Schematic illustration of the crosslinked polymer network induced by FRP and RAFT. b) Various RAFT agents used for tests. c) Mechanical properties of 3D printed materials with various RAFT agents (Zhang, *et al.*, 2021).

1.3.3. Visible-Light-Curable Adhesive

Light-induced photopolymerization is used for light-curable acrylic PSA, and a UV ray with a wavelength from 200 to 400 nm has been used mainly as a light source. However, there is a crucial advantage to using visible light instead of a UV ray in the light-curable PSA; polymerization is possible even under UV-blocked conditions (**Figure 1-18**).



Figure 1-18. Advantages of visible light curing: polymerization under UV-blocked conditions.

There are two examples of UV-blocked conditions. First, when a UVabsorbing material is placed on top of a light-curable PSA resin, the resin can be cured by visible light, not a UV ray. This situation may occur during the assembly process of a battery cell for an electric vehicle. In the process of adhering the battery cell to the polycarbonate bracket, a photocurable adhesive should be used. However, since polycarbonate is a UV-absorbing material, conventional UV-curable adhesives cannot be used. Henkel and Covestro developed a novel strategy to address this issue (Figure 1-19): Covestro manufactured UV-transparent polycarbonate by polymer blending (Bayblend®), and Henkel provided UV-curable acrylic adhesives with strong adhesive strength and short curing time: Loctite AA 3963 (Henkel, 2020). However, if visible-light-active photocatalyst-mediated photopolymerization is employed, it would be possible to attach the battery cell to a polycarbonate bracket without producing UV-transparent polycarbonate.



Figure 1-19. The schematic illustration of battery cell assembly uses visible light-curable adhesive (Henkel, 2020).

The second example of a UV-blocked condition is the polymerization of UVblocking PSA incorporating UV absorbers. UV-blocking PSA (precisely OCA) is a highly demanded material for current foldable mobile displays. Foldable displays have developed a new technology that reduces panel power consumption by eliminating polarizer film (Figure 1-20) (Kim, et al., 2011). Polarizer films were originally used to improve outdoor visibility, but they also block external UV rays to protect emitting layers (No, et al., 2016). Therefore, as the polarizer was removed, UV-blocking performance was required for other layers, and the demand for UV-blocking OCAs increased. In general, UV curing is widely used for OCA manufacturing (Behling, et al., 2016), but UV-blocking OCA has limitations in manufacturing via conventional UV-curing. Thermal curing could be an alternative process for manufacturing UV-blocking OCA (Shah, et al., 2019, Shitara, et al., 2017). However, it has several disadvantages, including increased thickness deviation, limitations in large-scale production, thermal-induced damage, and emission of volatiles. Therefore, visible-lightactive photocatalyst-mediated photopolymerization can be a powerful tool for preparing UV-blocking OCA (see below 3.4 in Chapter 3 for detail).



Figure 1-20. The device structure of foldable smartphones with a conventional display (left) and an advanced display (right).

However, visible light-curable adhesives have a significant drawback; poor transparency. Since the initiating materials for visible light-curing are colored, visible light-curable adhesives are inevitably colored. For example, LOCTITE[®] AA 3556TM, a commercially available adhesive, can be cured by visible light (> 400 nm), but it is yellow. Therefore, it has been used for medical devices rather than mobile displays requiring high transparency. For visible light-curable adhesives to be applied to mobile displays, it is essential to increase the efficiency of the initiating group and lower its contents to a minimum.

2. Objectives

Light-curable acrylic PSA has been extensively used in various fields, including mobile displays. Visible light-curing has significant benefits over UV-curing (light-curing ability in UV-blocked conditions), but the light source for light-curable acrylic PSA has been strictly limited to UV rays. Here, we developed visible-light-curable acrylic PSAs for mobile displays, and visible-light-active photocatalyst-mediated photopolymerization was employed (**Figure 1-21**). Although photocatalyst can initiate the polymerization with a smaller amount than PI, the content of photocatalyst should be further lowered for manufacturing optically transparent PSA for mobile displays. Therefore, increasing the photocatalyst's efficiency is essential to keep the polymerization rate fast even at low photocatalyst content.

We employed three strategies to address this issue; driving the catalytic cycle by 1) typical monomers used for acrylic PSAs or 2) additives. 3) Optimizing the catalytic cycle using various photocatalysts and additives. After that, considering various parameters and requirements, acrylic PSAs for display applications were adequately designed.

1) The catalytic cycle driven by typical monomers (precisely *N*-vinyl monomers) required a relatively large amount of photocatalyst. Therefore, the resulting PSAs were expected to be suitable for parts where transparency is not required (protection film-top, back film, and back plate). Furthermore, the adhesive strengths required for each layer are different, and monomer compositions of acrylic PSAs adjusted it.

2) Additives could drastically lower the photocatalyst content; thus, the manufactured PSAs were expected to apply to OCA (protection film, cover window, LR film). However, since the haloester-type additives we used could cause problems (generation of halogen gas and regulation of halogen), it was required to use another additive.

3) We finally optimized the photocatalyst and additives by screening various combinations. After that, UV-blocking OCAs were manufactured by adding UV absorbers into the optimized resin compositions. Their adhesive strength, viscoelasticity, and folding stability were evaluated for UV-blocking OCA to be applied for foldable displays.

PSA for mobile display



Advantages

- Usability in UV-blocked conditions Lower loading than PI
- Disadvantages

Slow curing rate >

Poor transparency

 Highly efficient catalytic cycle Requirements

Design of acrylic PSA

Parameters

- Monomer/additive compositions
 - \checkmark T_g, M_n, gel content

Requirements

- Fast curing rate
- Proper adhesive strength (for target layer)

 - High transparency (for OCA)
- Excellent folding stability (for foldable display)
- Excellent UV-protection (for UV-blocking OCA)





Figure 1-21. Schematic illustration of research objectives.

2.1. Driving the Catalytic Cycle by Typical Monomers for General PSA

We introduced three strategies to enhance the efficiency of the catalytic cycle and first employed the typical monomers used for conventional acrylic PSAs (Figure 1-22). N-vinyl-based monomers were chosen because they can improve the cohesive strength of PSAs and the efficiency of the catalytic cycle. We showed that tertiary amine in N-vinyl-based monomers could reduce the excited photocatalyst; thus, the reductive quenching cycle of photocatalyst could be driven. However, a relatively large amount of photocatalyst was required because of inefficient initiation between N-vinyl-based monomers and photocatalyst. Therefore, the resulting PSAs were suitable for PSAs in protection film, back film, and back plate rather than OCAs. For the resulting PSAs to be applied to them, the adhesive strength should be adjusted over a wide range. Viscoelasticity, mechanical strength and adhesion performance of acrylic PSAs were nicely adjusted in a broad range by controlling the acrylic monomer composition. In particular, the PSA with low $T_{\rm g}$ was found to be suitable for release film (protection film-top), and high $T_{\rm g}$ was found to be suitable for back film/plate that requires high adhesive strength.



Figure 1-22. Driving catalytic cycle by typical monomers (Back, et al., 2020).

2.2. Driving the Catalytic Cycle by Additives for OCA

In order to increase the initiation efficiency, additives were used as the second strategy. We employed oxidants (precisely α -haloester) that were already found to effectively drive the oxidative quenching cycle of photocatalyst (**Figure 1-23**). In the presence of α -haloester, the rate of film curing was greatly enhanced, which resulted in lowering photocatalyst loadings. Therefore, the resulting PSAs showed excellent transparency that could be used as OCA for display applications. However, α -haloester is a substance whose use in industry is regulated, and it could cause a problem, such as a generation of halogen gas when the PSA is exposed to heat. Therefore, we expected that it would be better to use another additive rather than α -haloester.



Figure 1-23. Driving catalytic cycle by additives (Back, et al., 2021).

2.3. Optimization of the Catalytic Cycle with Various Photocatalysts and Additives for UV-blocking OCA

We finally optimized photocatalysts and additives to drive a highly efficient catalytic cycle of the photocatalyst. Previously, we employed the oxidative quenching cycle, but here, the reductive quenching cycle was adopted for the following reasons; excluding halogen-based additives and granting oxygen tolerance. When the reductive quenching cycle was driven, this cycle could be facilitated by a tertiary amine, a commonly used organic compound. In addition, employing tertiary amine could grant oxygen tolerance in free-radical polymerization. Various photocatalysts and reductants were screened, and the best combination for driving the photocatalyst's reductive quenching cycle was obtained (Figure 1-24). This combination showed a fast polymerization rate and excellent oxygen tolerance even at low photocatalyst loading. Therefore, it was confirmed that the developed photocatalyst system was suitable for manufacturing OCAs. After that, UV absorbers were incorporated, and UVblocking OCAs were successfully manufactured. For UV-blocking OCAs to be applied to foldable displays, we optimized their viscoelasticity (storage modulus, Tg, strain recovery, and stress relaxation). As a result, the prepared OCAs showed excellent folding stability and satisfied most of the requirements for PSAs in foldable displays.



Figure 1-24. Optimization of the catalytic cycle with various photocatalysts/additives and preparation of UV-blocking OCA for foldable displays (Back, *et al.*, 2022).



Experimental Section

1. Materials

1.1. Photocatalysts

We employed various visible-light-active photocatalysts as follows;

- 4DP-IPN: 2,4,5,6-tetrakis(diphenylamino)isophthalonitrile
- 4Cz-IPN: 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile
- 4-o,p-DCDP-IPN: 2,4,5,6-tetrakis(2,4'-dicyanophenyl)isophthalonitrile
- 4-p,p-DCDP-IPN; 2,4,5,6-tetrakis(4,4'-dicyanophenylamino)isophthalonitrile

All photocatalysts were provided by Prof. Min-Sang Kwon, and their synthesis procedures are detailed in the reference (Back, *et al.*, 2022).



Figure 2-1. Various visible-light-active photocatalysts we used.

1.2. Acrylic Monomers

Several acrylic monomers and *N*-vinyl-based monomers were used; 2ethylhexyl acrylate (EHA, Aldrich), isobornyl acrylate (IBOA, Aldrich), acrylic acid (AA, Aldrich), 1-vinyl-2-pyrrolidinone (NVP, Junsei), *N*-vinylcaprolactam (NVC, Aldrich), butyl acrylate (BA, Aldrich), 4-hydroxybutyl acrylate (HBA, TCI), and poly(ethylene glycol) diacrylate (PEGDA, M_n: 700 g/mol, Aldrich). All monomers except for AA were purified by basic alumina (Aldrich). AA was purified by distillation.



Figure 2-2. Various acrylic monomers and N-vinyl-based monomers we used.

1.3. Others

Additives with oxidating/reducing ability were used to drive the catalytic cycle of visible-light-active photocatalysts. Three types of α -haloesters were employed as oxidant; diethyl 2-bromo-2-methylmalonate (DBM, Aldrich), ethyl 2-bromopropionate (EBP, Aldrich), and ethyl α -bromoisobutyrate(EBiB, Aldrich). Various reductants were employed to drive the reductive quenching cycle of the photocatalysts; 2-dimethylaminoethyl acrylate (DMAEA, Aldrich), 2-dimethylaminoethyl methacrylate (DMAEMA, Aldrich), 2-dimethylaminoethyl acetate (DMAEAc, TCI), *N*,*N*-dimethylbenzylamine (DMBA, TCI), triethylamine (TEA, Aldrich), and *N*,*N*-diisopropylethylamine (DIPEA, Aldrich).

Two types of UV absorbers were simultaneously used for manufacturing UV-blocking OCAs. We purchased ethyl 2-cyano-3,3-diphenylacrylate (Aldrich) and used it as UV absorber 2. UV absorber 1 was Dimethyl 2-(4-(dimethylamino)benzylidene)malonate), and it was synthesized as follows; 4.87 g of dimethyl malonate and 5.00 g of 4-(dimethylamino)benzaldehyde were dissolved in 50 mL of methanol. We added 0.45 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene, and stirred the solution at ambient temperature for one day. After thickening the mixture under reduced pressure, it was poured into 100 mL of distilled water. The mixture was then filtered to remove a precipitate and washed (water, methanol). Finally, after vacuum drying, 7.54 g of product (yield: 85.5%) was obtained. The chemical structure of UV absorber 1 was confirmed by ¹H-NMR (300 MHz, DMSO-d₆); δ 7.58 (s, 1H), 7.37 – 7.23 (d, 2H), 6.80 – 6.67 (d, 2H), 3.81 (s, 3H), 3.73 (s, 3H), 2.99 (s, 6H).



Figure 2-3. ¹H NMR result of UV absorber 1 (DMSO-d₆) (Back, et al., 2022).

2. Preparation of Acrylic PSAs

2.1. Bulk Polymerization

Visible-light-curable acrylic PSAs were prepared by following two steps; bulk polymerization and film curing (**Figure 2-4**). First, acrylic monomers were mixed with photocatalyst and additives (*N*-vinyl-based monomer, oxidant, or reductant), and the mixture was degassed by Argon purging. Then, bulk polymerization was conducted by irradiating blue light. Two Bulb-type blue LEDs were used for bulk polymerization; "Bulk polymerization set-up 1" (456 nm, 5 mW/cm²) was used for *1.2 and 2.2 in Chapter 3*, while "Bulk polymerization set-up 2" (455 nm, 100 mW/cm²) was used for *3.1, 3.2, and 3.4 in Chapter 3*.



Figure 2-4. Example of the PSA manufacturing process using visible-lightactive photocatalyst-mediated photopolymerization: Bulk polymerization (left) and film curing (right) (Back, *et al.*, 2021).

The molecular weight of the acrylic pre-polymer obtained by bulk polymerization was evaluated using size-exclusion chromatography (SEC). Test conditions of SEC were slightly different as follows;

• For 1.2 in Chapter 3

: equipment (1260 Infinity || LC, Agilent technologies, chamber temperature: 40°C, detector: reflex index detector), eluent (tetrahydrofuran, 1 mL/min), calibration (polystyrene), column (used an old column because of high polarity of the pre-polymer).

• For 2.2 in Chapter 3

: equipment (1260 Infinity || LC, Agilent technologies, chamber temperature: 40°C, detector: reflex index detector), eluent (tetrahydrofuran, 0.5 mL/min), calibration (polystyrene), column (ShodexTM KF-G, 602, 604, and 605).

• For 3.2 in Chapter 3

: equipment (1260 Infinity || LC, Agilent technologies, chamber temperature: 40°C, detector: reflex index detector), eluent (tetrahydrofuran, 1 mL/min), calibration (poly(methyl methacrylate)), column (ShodexTM KF-G, 803, 804, and 805).

Since the polymers do not vaporize at 120°C, conversion of bulk polymerization was evaluated by the solid content of the acrylic pre-polymer (for 2.2 and 3.2 in **Chapter 3**). In addition, conversion was also assessed using ¹H-NMR (for 1.2 in **Chapter 3**, 300 MHz, Avance DPX-400, Bruker, CDCl₃). The monomers' proton peak (A_{mon}) integration was reduced after the bulk polymerization (**Figures 2-5** and **2-6**). Therefore, the conversion (α_{mon}) of the bulk polymerization could be calculated by calculating the reduction gap of A_{mon} . The certain proton peak of EHA was chosen as the standard peak for the following reasons; there was no significant difference in the peak before/after bulk polymerization, and the peak was not overlapped with other peaks. The conversion (α_{mon}) was calculated by the following equation;

$$\alpha_{mon} (\%) = \frac{A_{mon}/A_{std} - A'_{mon}/A'_{std}}{A_{mon}/A_{std}} \times 100$$

(A means peak integration; A_{mon}; monomer/before bulk polymerization, A_{std}; standard/before bulk polymerization, A'_{mon}; monomer/after bulk polymerization, and A'_{std}; standard/after bulk polymerization)

Additionally, the bulk polymerization's total conversion (α_t) was obtained as follows;

$$\alpha_t = \sum x_{mon} \cdot \alpha_{mon}$$

 $(x_{mon} means monomer's mole fraction)$

Since the viscosity of the pre-polymer resin is determined by its molecular weight and conversion after bulk polymerization, reaction time should be carefully adjusted. For example, the conversion should be lowered to obtain the pre-polymer with suitable viscosity for film coating when the molecular weight is large. In other words, if the molecular weight and conversion are both too high or too low, the resulting pre-polymer cannot be coated in a film form.
a. 2-Ethylhexyl acrylate





b. Isobornyl acrylate



12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 Chemical shift (ppm) 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

c. 1-Vinyl-2-pyrrolidinone



10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 Chemical shift (born) 12.5 11.5

Figure 2-5. ¹H-NMR result of monomers we used (a-e) (Back, et al., 2020).



Figure 2-6. Example of ¹H-NMR: a) before and b) after bulk polymerization (Back, *et al.*, 2020).

2.2. Film Curing

Acrylic pre-polymers were obtained by bulk polymerization, and the crosslinking agent (PEGDA) was added to the pre-polymers. Then, the mixture was coated on the backing film and cured with blue light. The thickness of the PSA was set as follows; 120 μ m (for *1.2 and 1.3 in Chapter 3*), 100 μ m (for *2.2 and 2.3 in Chapter 3*), and 50 μ m (for *3.1, 3.2, 3.3, and 3.4 in Chapter 3*). Two or three string-type blue LEDs were used for film curing; "Film curing set-up 1" (three strings, 448 nm, 0.3 mW/cm²) was used for *1.2, 1.3, 2.2 and 2.3 in Chapter 3*, while "Film curing set-up 2" (two strings, 452 nm, 15 mW/cm²) was used for *3.1, 3.2, 3.3, and 3.4 in Chapter 3*.

Conversion of the film curing was calculated using Fourier-transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Fisher Scientific, attenuated total reflectance (ATR) mode, scan number: 16) and the following equation;

Conversion (%) =
$$\frac{A_{0(C=C)}/A_{0(C=O)} - A_{t(C=C)}/A_{t(C=O)}}{A_{0(C=C)}/A_{0(C=O)}}$$

(*A* means peak integration; $A_{0(C=O)}/A_{t(C=O)}$ mean the carbonyl peak (1760-1660 cm⁻¹) before/after film curing, respectively. $A_{0(C=C)}/A_{t(C=C)}$ mean the C=C peak (peak area of carbonyl (830-790 cm⁻¹ for *1.2, 3.2 and 3.4 in Chapter 3*, 1660-1600 cm⁻¹ for *2.2 in Chapter 3*) before/after film curing, respectively.)



Figure 2-7. Example of evaluating film curing conversion by FT-IR (Back, *et al.*, 2022).

3. Characterization of Acrylic PSAs

3.1. Gel Content

Crosslinking degree of the prepared acrylic PSA was evaluated by gel content. Gel content means the weight fraction of crosslinked polymers to the overall cured PSA. Gel content was evaluated by the following steps; the cured PSA was dissolved in toluene to separate linear and crosslinked polymer. The crosslinked polymer cannot be dissolved but is swollen. On the other hand, the linear polymer is perfectly dissolved by toluene. Then, the crosslinked polymer can be separated by steel mesh (#200). The gel content was calculated as follows, and the gel content was evaluated three times per sample.

Gel content (%) =
$$\frac{W_{mesh+residue} - W_{mesh}}{W_{total polymer}} \times 100$$

(W means weight. $W_{\text{mesh+residue}}$: mesh with crosslinked polymer after drying,

 W_{mesh} : mesh, and $W_{\text{total polymer}}$: total weight)

3.2. UV/Vis Spectroscopy

The prepared PSA's transparency, light absorption, and UV-protection ability was evaluated using UV/Vis spectroscopy (UV-3600, Shimadzu). Coronatreated polyethylene terephthalate film (PET_f, 50 μ m-thick, Youngwoo Trading, *for 2.3. in Chapter 3*) or quartz cells (for others) were used as reference substrates. UV/Vis spectroscopy experiment was conducted without repetitions.

3.3. Adhesive Performances

3.3.1. 180° Peel Test

Specimens for evaluating PSA's adhesive performances were cured using corona-treated PET_f and silicone-treated PET_f (50 μ m-thick, Youngwoo Trading) as bottom and top film, respectively. The cured specimens were cut to have a specific width (1 cm). Then, the cut specimens were attached to the substrates (SUS304 or glass) by 2 kg roller (rolling for two round trips). After one day, the force was measured while peeling the specimen from the substrate in the direction of 180 degrees (universal testing machine, UTM, LS1, AMETEK, 10 kgf load cell). Peel strength was obtained as the average force from 20% to 80% of the operating range (**Figure 2-8**). The 180° peel test was repeated 4~5 times for each test.



Figure 2-8. Schematic illustration for 180° peel test (Back, et al., 2020).

3.3.2. Loop Tack Test

Specimens for evaluating loop tack were prepared the same way as the 180° peel test. In addition, the specimens were cut one more to have a 15 cm length. The string-shaped PSA specimen approached the substrate (SUS304 or glass) with a fixed crosshead speed (5 mm/s). The specimen was immediately detached after contact with the substrate at a constant speed (5 mm/s). Force was also obtained by UTM (LS1, AMETEK, 10 kgf load cell), and a maximum force was recorded as a loop tack (**Figure 2-9**). The loop tack test was repeated 4~5 times for each test.



Figure 2-9. Schematic illustration for loop tack test (Back, et al., 2020).

3.3.3. Lap Shear Test

The cohesive strength of the prepared PSAs was evaluated by the lap shear test or holding test. The PSA was cured between a release film (silicone-treated PET_f) and a backing film (corona-treated PET_f), and the specimens were cut to have a 25 mm width. The specimen was attached to another corona-treated PET_f by 2 kg roller (rolling for two round trips), and the bonding area was fixed as 25 mm X 25 mm. After one day, the force was measured while peeling the specimen in a tensile direction, as shown in **Figure 2-10** (UTM, LS1, AMETEK, 10 kgf load cell). Maximum stress was recorded as a lap shear strength, and the lap shear test was repeated $4\sim5$ times for each test.



Figure 2-10. Schematic illustration for lap shear test (Back, et al., 2020).

3.3.4. Holding Test

The PSA was cured between silicone-treated PET_f and corona-treated PET_f , and the cure specimens were cut to have a 15 mm width. Then, the specimen was attached to the substrate (SUS 304) by 2 kg roller (rolling for two round trips). The adhesion area was fixed as 15 m X 15 mm, and the holding test was assessed one hour after attachment. Next, a 1 kg weight was connected to the specimen (**Figure 2-11**), and the time was measured for how long it lasted. The temperature was set as 50°C. There was no repeated number for the holding test, and holding time was obtained by a single experiment.



Figure 2-11. Picture of holding test (Back, et al., 2021).

3.4. Viscoelasticity

3.4.1. Viscoelastic Window (Frequency-Sweep)

In general, the performances of PSAs strongly depend on their viscoelasticity. Therefore, the possible application of the prepared PSAs can be roughly expected via their viscoelastic window. From the values of storage modulus (G') and loss modulus (G'') at bonding frequency (0.01 Hz) and debonding frequency (100 Hz), the viscoelastic window of PSA can be drawn as shown in **Figure 2-12** (Chang, 1991, Chang, 1997). For example, if the viscoelastic window of a PSA belongs to region 4, such a PSA will show a high potential to be used as a unique PSA for low-temperature conditions.



Figure 2-12. The viscoelastic window of PSAs (Chang, 1991, Chang, 1997).

The viscoelasticity of the prepared PSA was evaluated using dynamic mechanical analysis (DMA, Q800, TA Instrument) with a shear sandwich clamp (**Figure 2-13**). Several PSA layers were stacked to a specific thickness ($0.5 \sim 1$ mm) to prepare DMA specimens. The width and length of the DMA specimens were set as 10 mm. For the construction of the viscoelastic window, the frequency-sweep test was conducted ($0.01 \text{ Hz} \sim 100 \text{ Hz}$) at a fixed temperature (23° C). The applied strain was set as 1%. The viscoelasticity test was conducted as a single experiment without repetitions.



Shear sandwhich clamp

Figure 2-13. The shear sandwich clamp of DMA (Back, *et al.*, 2020, Back, *et al.*, 2022).

3.4.2. Temperature Sweep

For a temperature-sweep test, all test set-ups except for temperature and frequency conditions were the same as the frequency-sweep test. The frequency was set as 1 Hz, and the temperature increased from -80°C to 100°C with a fixed increasing rate (3°C/min).

3.4.3. Strain Recovery and Stress Relaxation

The cured PSA's flexibility (strain recovery and stress relaxation) was assessed using DMA at ambient temperature (23°C). Specimens and clamps were the same as the frequency or temperature-sweep test. The applied strain, displacement, and recovery time were set as 300%, 10 min, and 5 min, respectively. Strain recovery and stress relaxation were obtained, as shown in **Figure 2-14**.



Figure 2-14. Examples of a) strain recovery curve and b) stress relaxation curve (Back, *et al.*, 2022).

3.5. Folding Stability

3.5.1. Preparation of the Test Specimens

The folding stability of the prepared PSAs was evaluated by a dynamic folding test. Test specimens were designed concerning the actual foldable display structure (**Figure 2-15**), and this specimen structure has been widely used in the foldable display industry (Campbell, *et al.*, 2017). In this specimen structure, colorless polyimide film (colorless polyimide; CPI, 50 μ m) and yellow polyimide film (PI_f, 50 μ m) were used, and our PSAs were positioned between CPI and yellow polyimide film (PI_f). The test specimen's size was 160 mm X 20 mm. An autoclave was used to prevent the generation of air bubbles during the stacking process, and the autoclave condition was as follows; equipment (P01-400-16-120, PHOS-ENTECH), temperature (50 °C), pressure (5 bar), and time (10 min for increasing temperature/pressure and 30 min for fixed temperature/pressure).

3.5.2. Dynamic Folding Test

Customized equipment (Foldy-200, FlexiGO) was employed to conduct the dynamic folding test (**Figure 2-16**). Folding proceeded in the in-fold direction, and the frequency/curvature radius was set as 0.5 Hz/1.5 mm. Three different test conditions were employed to evaluate folding stability as follows;

- Room temperature: 25°C, 200,000 cycles
- Low temperature: -20°C, 30,000 cycles
- High temperature/high humidity: 60°C/93%, 50,000 cycles



Figure 2-15. Structure of a) actual foldable display and b) test specimen we used (Back, *et al.*, 2022).



Figure 2-16. a) Outside and b) inside view of the equipment for the dynamic folding test. c) Scheme for the in-fold test procedure. d) Pictures of the folding plate (w/o specimen, side view, top view, and set test view) (Back, *et al.*, 2022).

3.5.3. Evaluation of the Folding Stability

From the dynamic folding test, the folding stability was quantitatively and qualitatively evaluated (**Figure 2-17**). For quantitative evaluation, the surface texture change (ΔZ) was estimated. In addition, the folding stability was quantitatively evaluated by observing the appearance of test specimens after folding. The dynamic folding test experiments were repeated twice for all entries.



Figure 2-17. a) Schematic illustration for the dynamic folding test. b) Quantitative evaluation of the folding stability by the change in surface texture (ΔZ). c) Qualitative evaluation of the folding stability by observing defects on the specimens (Back, *et al.*, 2022).



Results and Discussion

1. Driving the Catalytic Cycle by Typical Monomer for General PSA

1.1. Strategy

Previous studies have found highly efficient organic photocatalysts via a computer-aided design (Singh, *et al.*, 2018, Song, *et al.*, 2019). Among them, 4DP-IPN was the most efficient for the following reasons: 1) superior photo/electrochemical stability, 2) strong absorption of visible light, 3) suitable redox potentials, and 4) excellent triplet generation. The polymerization of methyl methacrylate (MMA) could be successfully controlled even at a low photocatalyst loading (0.5 ppm). Therefore, 4DP was employed as a photocatalyst for preparing visible-light-curable acrylic PSAs.

Acrylic PSAs generally consist of various acrylic monomers, and monomers with functional groups usually enhance the cohesive strength of the PSAs. Among them are monomers containing tertiary amine, which can be used as reducing agents. For example, *N*-vinyl-based monomers contain tertiary amine and vinyl groups, acting as a reducing monomer (monomer with reducing ability). Therefore, we expected that employing *N*-vinyl-based monomers in PSA could facilitate the reductive quenching cycle of the 4DP-IPN, speeding up the polymerization rate. In addition, it was also expected that the cohesive strength of the PSAs could be enhanced by employing *N*-vinyl-based monomers, and various PSAs could be manufactured by adjusting the other monomer compositions.

1.2. Preparation of Visible-Light-Curable Acrylic PSAs

1.2.1. Bulk Polymerization

In order to manufacture visible-light-curable acrylic PSAs, the first step was the photo-induced bulk polymerization of acrylic monomers (**Figure 3-1**). In a control experiment, acrylic monomers (EHA, IBOA, AA) were polymerized under an Ar condition by UV irradiation (*entry control in* **Table 3-1**). We employed commonly used monomer composition for light-curable acrylic PSAs. The "entry control" produced acrylic pre-polymer with sufficient conversion ($\alpha_t = 14.4\%$) and molecular weight ($M_n = 664$ kg/mol) in 30 seconds, and the prepared pre-polymer exhibited a suitable viscosity for the film casting.

After that, visible-light-active photocatalyst-based bulk polymerization was conducted using 50 ppm of 4DP-IPN. The polymerization was carried out by irradiating blue light (5 mW/cm²) under Ar condition (*entry 2 in* **Table 3-1**). The pre-polymer was produced with sufficient conversion ($\alpha_t = 9.9\%$), and molecular weight (M_n = 948 kg/mol). However, a much longer irradiation time (280 s) was required for bulk polymerization. This poor polymerization rate was ascribed to an ineffective initiation caused by the lack of α -haloester and sacrificial electron donors (e.g. DIPEA). These additives are frequently required for photocatalyst-based free radical polymerization (K1z1lel, et al., 2004, Nomeir, et al., 2019, Zhang, et al., 2011).



Figure 3-1. Procedure for preparing visible-light-curable acrylic PSAs using photocatalyst and *N*-vinyl-based monomer (Back, *et al.*, 2020).

In previous studies, the polymerization rate and the conversion of photoinduced polymerization significantly increase by NVP (Aguirre-Soto, et al., 2019, White, et al., 2006, White, et al., 2007). Several explanations have been presented to explain such polymerization rate increases, but the conclusion remains rather contentious. We expected that NVP could increase the polymerization rate, and the polymerization behaviors with different content of NVP were studied. The total molar fraction of IBOA/NVP was set as 30 mol% to minimize the difference in T_g of the resulting PSAs because the adhesive strength of the PSAs drastically decreased when the T_g of PSAs was too high.

The results of the bulk polymerization in the presence of NVP are shown in **Table 3-1**, and the optimum content of 4DP-IPN was determined to be 50 ppm (entries 5, 10, and 11). As predicted, the bulk polymerization rate rose significantly as the quantity of NVP increased *(entries 2, 4-7 in Table 3)*. Surprisingly, increasing the quantity of NVP resulted in a considerable drop in the molecular weight. This result suggested that NVP may operate as an initiator (**Figure 3-2**). However, given the NVP concentration as well as the molecular weight, only a tiny amount of NVP may be engaged in the initiation step.

Table 3-1. Results of the bulk polymerization (Back, *et al.*, 2020). The total conversion of bulk polymerization (α_t) was characterized by ¹H-NMR (*see* **Figures 2-5** *and* **3-6**). M_n was characterized by SEC. \oplus represents dispersity.

Entry	[IBOA]:[NVP]:[4DP-IPN] ^a	Time (s)	α_{t} (%)	$M_n(kg\!/mol)$	Ð
Control ^b	30:0:0.045	30	14.4	665	1.77
1	30:0:0	> 4,200	0	-	-
2	30:0:0.005	280	9.9	948	1.52
3	20:10:0	> 4,200	0	-	-
4	25:5:0.005	220	11.3	709	1.74
5	20:10:0.005	145	10.6	655	1.64
6	10:20:0.005	90	10.9	353	1.82
7	0:30:0.005	60	13.4	143	2.32
8 ^c	0:30:0.005	720	0	-	-
9 ^d	0:30:0.005	60	3.9	394	2.11
10	20:10:0.0005	520	9.5	510	1.65
11	20:10:0.05	1,160	12.9	688	1.84
12 ^e	20:10:0.005	170	9.1	560	1.81

^a[EHA]:[AA] = 65:5. ^bUV-active PI (450 ppm) was used instead of a photocatalyst. ^cNo Ar purging. ^d Presence of inhibitor (MEHQ, 0.3 wt%). ^{e)} NVC was used instead of NVP.

Entry	Reaction time (s)	α_{t} (%)	M _n (kg/mol)	Đ
	320	7.53	897	1.54
	280	9.85	948	1.52
	260	6.45	967	1.52
2	260	8.01	945	1.58
	15	21.78	352	2.07
	13	17.64	350	2.09
	12	12.52	278	2.28
	300	12.19	590	1.94
4	220	11.27	709	1.74
4	210	8.90	726	1.74
	210	9.16	622	1.54
	275	12.99	491	1.89
	145	10.56	655	1.64
5	145	7.73	497	2.11
5	145	7.40	694	1.66
	130	10.27	653	1.64
	100	10.91	674	1.61
	115	10.47	335	1.82
6	105	9.01	309	1.90
0	90	10.85	353	1.82
	85	10.50	330	1.76
	70	10.38	154	2.15
7	60	12.98	164	2.06
/	60	13.40	143	2.32
	53	12.66	154	2.07
	600	10.23	563	1.75
	520	9.53	510	1.65
	360	8.97	628	1.69
10	250	10.12	629	1.63
	320	10.45	588	1.63
	320	10.86	642	1.55
	240	9.79	531	1.65
	1575	14.85	559	2.07
	1160	12.90	688	1.84
11	990	10.66	398	1.98
11	990	9.19	515	2.32
	973	11.54	679	1.86
	850	10.66	616	1.96
12	125	7.27	647	1.69
12	170	9.07	560	1.81

Table 3-2. Reproducibility test results of Table 3-1 (Back, et al., 2020).



Figure 3-2. Proposed mechanism for initiation via NVP and 4DP-IPN (Back, *et al.*, 2020).

Our coworker analyzed the HOMO energy levels of photocatalyst (4DP-IPN) and monomers (NVP and methyl acrylate; MA) to identify the causes of an inefficient initiation process (**Figure 3-3a** and **b**). The HOMO level was higher for NVP (1.56 eV) than MA; thus, an electron transfer from the monomer to the excited 4DP-IPN was faster for NVP than MA. Furthermore, it was demonstrated that an electron transfer from NVP to NVP was an endothermic process (**Figure 3-3c**). Therefore, only a very minimal quantity of NVP is predicted to engage in the initiation step, and this result supported the bulk polymerization results. In addition, this result is also supported by the excited state reduction potentials (E_{red}^*); singlet and triplet E_{red}^* of 4DP-IPN (0.93 and 0.76 V) are similar to 1.1 V (critical voltage for NVP's electrochemical polymerization) (Doneux, *et al.*, 1997).



Figure 3-3. a) Molecular orbital diagram of photocatalyst (4DP-IPN) and monomer (NVP and MA). b) Chemical structures of monomer (NVP and MA). c) Scheme for an electron transfer from NVP (S₀) to 4DP-IPN (T₁) (Back, *et al.*, 2020).

For the preparation of light-curable acrylic PSAs, conventional UV-active PIs should be added to both bulk polymerization and film curing because most PIs are consumed at the bulk polymerization step. However, since the photocatalyst can be regenerated by the catalytic cycle, adding the photocatalyst to the film curing step is unnecessary. It was confirmed by UV/Vis spectroscopy that the photocatalyst was not consumed in the bulk polymerization step (**Figure 3-4**). Monomers ([EHA]:[AA]:[IBOA]:[NVP] = 65:5:20:10) and photocatalyst (4DP-IPN, 50 ppm) were mixed, and the mixture was dissolved in ethyl acetate (5% v/v). As a result of the experiment, there was no significant difference in UV/Vis spectra before and after bulk polymerization. Therefore, it was found that most of the photocatalyst was regenerated rather than consumed. photocatalyst



Figure 3-4. UV/Vis spectra of the monomer solution (before and after bulk polymerization (Back, *et al.*, 2020).

1.2.2. Film Curing

Next, the visible-light-curing behavior of the pre-polymer was studied. For the film curing, 1 wt% of crosslinking agent (PEGDA) was added to the prepolymer, and the mixture was coated in a film form. Conversion of film curing was evaluated as a function of irradiation time. Film curing proceeded as predicted without additional photocatalyst and/or PIs. As expected, the curing rate significantly increased with increasing content of NVP (**Figure 3-5**) and 4DP-IPN (**Figure 3-6**). Despite this increase, the curing rate remains much slower than conventional UV-curing (**Figure 3-7**). We ascribed this mainly to the light source's low intensity, and a light source with high intensity can further improve the curing rate.



Figure 3-5. Conversion of film curing as a function of irradiation time for different NVP content (*entries 2 and 4-7 in* **Table 3-1**) (Back, *et al.*, 2020).



Figure 3-6. Conversion of film curing as a function of irradiation time for different 4DP-IPN content (*entries 5, 10, and 11 in* Table 3-1) (Back, *et al.*, 2020).



* Minimum irradiation time for film formation

* Maximum conveyor speed for film formation

Figure 3-7. a) Schematic illustration for the film curing using UV-active PI (Irgacure 184). Conversion of the film curing using b) low-intensity UV light (UV blacklight, 20 mW/cm²) and c) high-intensity UV light (UV metal halide, 300 mW/cm^2) (Back, *et al.*, 2020). In the case of high-intensity UV, curing was completed within one minute, and it is not easy to accurately calculate the irradiation time from the conveyor speed.

1.3. Characterization of Visible-Light-Curable Acrylic PSAs

1.3.1. Viscoelasticity

The viscoelastic characteristics of PSAs should be characterized since the adhesive performances (tack, peel, and shear strength) are heavily dependent on them (Chang, 1991, Satas, 1999). Hence, we evaluated the viscoelasticity of our PSAs via a frequency-sweep test (*see 3.4.1 in Chapter 1*), and drew viscoelastic windows.

Six distinct PSAs were manufactured by considering the parameters (T_g and content of polar monomer) known to impact the PSA's viscoelasticity (**Table 3-3**). Six entries had different acrylic monomer compositions (EHA, AA, and IBOA), and the contents of NVP and PEGDA were set as 10 mol% and 1 wt%, respectively. Notably, 10 mol% of NVP should be incorporated to enhance the polymerization rate and conversion. However, despite the use of NVP, the particular composition exhibited a slow polymerization rate (*entry 6 in* **Table 3-3**). This result suggested that more studies into the mechanism of NVP-mediated polymerization are required.

Table 3-3. Bulk polymerization results in different monomer compositions (Back, *et al.*, 2020). The total conversion of bulk polymerization (α_t) was characterized by ¹H-NMR (*see* Figures 2-5 *and* 3-6). $T_{g,cal}$; expected T_g calculated by Flory-Fox equation. $T_{g,exp}$; T_g obtained by differential scanning calorimetry (*see Figure 3-8 below*).

Entry	[EHA]:[AA]:[IBOA] ^a	T _{g,cal} (°C)	T _{g,exp} (°C)	Time (s)	α _t (%)	Mn (kg/mol)	Ð
1	50:10:30	-17.6	-22.3	170	11.60	156	3.23
2	50:5:35	-12.1	-30.3	130	11.65	336	1.95
3	60:5:25	-30.1	-34.4	115	9.11	512	1.78
4	70:5:15	-44.0	-42.2	130	10.12	740	1.72
5	80:5:5	-56.8	-49.7	115	8.68	573	1.69
6	90:0:0	-65.0	N/A	1273	9.44	1,075	1.61

^a[NVP]:[Photocatalyst]=10:0.005.

Entry	Reaction time (s)	a _t (%)	$M_n \left(kg/mol \right)$	Đ
	185	12.14	172	2.98
1	170	11.60	156	3.23
	160	11.40	162	3.03
	130	11.86	454	1.94
2	130	11.65	336	1.95
	115	10.31	373	1.91
	140	10.08	498	1.85
3	115	9.11	512	1.78
	110	10.94	427	1.83
	135	9.30	701	1.72
4	130	10.12	740	1.72
4	125	9.05	696	1.75
	120	9.15	727	1.63
5	115	8.68	573	1.69
5	110	8.87	476	1.71
	1290	8.67	1,167	1.51
C.	1273	9.44	1,075	1.61
0	1130	7.53	981	1.68
	1030	13.11	897	1.79

Table 3-4. Reproducibility test results of Table 3-3 (Back, et al., 2020).



Figure 3-8. Examples of heat flow curves obtained by differential scanning calorimetry (Back, *et al.*, 2020). Test conditions; sample (*entries 1, 4, and 6 in* **Table 3-3**, 9-10 mg), 1st scan (from 25 to 100 °C, 20 °C/min), cooling (from 100 to -70 °C, -20 °C/min), 2nd scan (from -70 to 40 °C, 5 °C/min).

As predicted, storage modulus rose as the quantity of high T_g monomer (IBOA and NVP) increased (**Figure 3-9a** and **b**). The prepared PSAs did not cover regions 3 and 4, which other PSAs can cover, such as silicone PSAs (**Figure 3-9c** and **d**) (Chang, 1991). Although the produced PSAs were unable to cover certain regions due to inherent limited physical properties, the G' of acrylic PSAs could be adjusted across an extensive range, mostly covering regions 1, 2, and 5. As a result, the produced PSAs can be employed in most situations where traditional acrylic PSAs are used (release coatings, general-purpose PSA, and high-shear PSA) (Chang, 1991, Gallagher, *et al.*, 2016).



Figure 3-9. a) Frequency-storage modulus curve and b) viscoelastic window of various PSAs (*entries 1-6 in* **Table 3-3**). c) Frequency-storage modulus curve and d) viscoelastic window of acrylic PSAs with different NVP content (*entries 2, 4-7 in* **Table 3-1**). The irradiation time of blue LED for film curing was set as 60 min for all PSAs (Back, *et al.*, 2020).
1.3.2. Physical Properties and Adhesive Performances

At last, we evaluated the physical properties and adhesive performances (**Table 3-5**). All PSAs exhibited sufficient conversion of film curing (> 86%) and gel content (88.3~95.0%). The proportion of high T_g monomers (IBOA and NVP) enhanced both the lap shear strength and elongation at break, implying that the monomer composition may readily modify the toughness of PSAs (**Figure 3-10** and **3-11**, **Table 3-5** and **3-6**). The produced PSAs' lap shear strengths (0.189~0.254 MPa) were in good agreement with those of the previously published photo-responsive acrylic adhesives (0.150~0.341 MPa) (Harper, *et al.*, 2017, Kim, *et al.*, 2017).



Figure 3-10. a) Strain-stress curve of lap shear test, b) extension-force curve from 180° peel test (substrate: stainless steel), and c) extension-force curve from loop tack test of various PSAs (substrate: stainless steel, *entries 1-6 in* **Table 3-3**). The irradiation time of blue LED for film curing was set as 60 min for all PSAs (Back, *et al.*, 2020).

Two types of substrates, *i.e.*, stainless steel and glass, were employed to conduct 180° peel and loop tack tests. The produced PSAs showed higher loop tack when glass was used as substrate than stainless steel. This result was caused by higher surface energy and lower roughness of glass, which improve the wettability of the PSA (Kowalski, *et al.*, 2015). On the other hand, stainless steel had a higher peel strength. This difference may result from stainless steel's rough surface and better mechanical interlocking of the PSA. The PSA with the highest peel strength (*entry 1 in* **Table 3-5**) exhibited low loop tack value and showed stick-slip behavior during a debonding experiment (**Figure 3-10b**, dark grey line) because of its too high T_g .

In conclusion, although the prepared PSAs showed poor transparency because of the high loading of 4DP-IPN (50 ppm, **Figure 3-12**), certain compositions had sufficient peel strength (4.17~4.59 N/cm) and loop tack (3.35~4.59 N/cm). Those values are equivalent to commercially available PSAs like duct tape (peel strength: 4 N/cm, tack: 5 N/cm) (Beharaj, *et al.*, 2019, Sulley, *et al.*, 2020). In addition, PSA with the lowest peel strength (0.40 N/cm) was suitable for release film (protection film-top) in displays. On the other hand, PSA with the highest peel strength (9.90 N/cm) was suitable for adhesion of the back film/plate in displays.



Figure 3-11. a) Strain-stress curve of lap shear test, b) extension-force curve of 180° peel test, and c) extension-force curve of loop tack test of PSAs with different NVP content (*entries 2, 4, 5, 6, and 7 in* **Table 3-1**). Stainless steel substrates were used for peel strength and loop tack. The irradiation time of blue LED for film curing was set as 60 min for all PSAs (Back, *et al.*, 2020).

Table 3-5 . Lap shear strength, elongation at break, peel strength, loop tack, gel fraction, and film conversion of various DSAs (surface) 1 & in Table 3 3). The imposition time of blue I ED for film annian mass for an film for all DSAs (surface).
(Back, et al., 2020). (In Table 3-3), The internation units of other LED for thin curing was set as ov thin for an F3As

	Lap shear	Elongation	Peel s (N)	trength /cm)	L00] (N)	p tack (cm)	Film	Gel
Entry	strengtn (MPa)	at break (mm/mm)	Stainless steel	Glass	Stainless steel	Glass	conversion (at, %)	Iraction (%)
-	0.242 (±0.007)	47.50 (±5.64)	9.90ª (±1.12)	5.87 (±0.34)	1.15 (± 0.30)	5.59 (±0.45)	90.6	90.8
7	0.254 (±0.013)	42.36 (±2.25)	4.51 (±0.31)	4.73 (±0.16)	4.59 (±0.69)	7.51 (±0.57)	86.3	88.8
ŝ	0.246 (±0.007)	37.89 (±3.55)	4.17 (±0.37)	3.52 (±0.24)	5.15 (±0.57)	7.63 (±0.44)	90.3	92.4
4	0.224 (±0.003)	26.71 (±2.79)	4.59 (±0.16)	2.56 (±0.11)	3.35 (±0.18)	4.39 (±0.47)	90.8	88.3
S	0.228 (±0.009)	28.34 (±3.03)	2.05 (±0.15)	1.59 (± 0.09)	3.38 (±0.36)	4.56 (±0.43)	94.4	95.0
9	0.189 (±0.014)	13.62 (±0.98)	0.40 (±0.08)	$0.26 (\pm 0.04)$	$1.98 (\pm 0.28)$	2.17 (±0.59)	93.3	93.2
Stick-slip w	as observed in a	debonding experin	ient.					

Table 3-6. Lap shear strength, elongation at break, peel strength, and loop tack of various PSAs (*entries 2, 4, 5, 6, and 7 in* **Table 3-1**). The irradiation time of blue LED for film curing was set as 60 min for all PSAs (Back, *et al.*, 2020).

Entry	Lap shear strength	Elongation at break	Peel strength	Loop tack
	(MPa)	(mm/mm)	(N/cm)	(N/cm)
2	0.219	27.29	3.42	5.57
	(±0.033)	(±7.40)	(±0.10)	(±1.88)
4	0.249	39.83	3.30	5.20
	(±0.005)	(±1.75)	(±0.07)	(±0.69)
5	0.250	47.38	6.64	7.18
	(±0.007)	(±4.16)	(±0.38)	(±0.17)
6	0.254	52.93	7.48	6.34
	(±0.007)	(±3.90)	(±0.36)	(±1.09)
7	0.264	72.67	7.74	5.99
	(±0.012)	(±3.24)	(±0.20)	(±0.32)



Figure 3-12. Picture of the prepared PSAs using 50 ppm of 4DP-IPN (Back, *et al.*, 2020).

1.4. Conclusions

Here, we successfully manufactured visible-light-curable acrylic PSA using a photocatalyst and a typical monomer, driving the reductive quenching cycle of the photocatalyst. 4DP-IPN was selected as photocatalyst for the following advantages; 1) superior photo/electrochemical stability, 2) strong absorption of visible light, 3) suitable redox potentials, and 4) excellent triplet generation. Visible-light-curable acrylic PSAs were manufactured in two steps; bulk polymerization and film curing. It was discovered that N-vinyl-based monomers significantly increased the polymerization rate. Furthermore, we showed that N-vinyl-based monomers initiated the polymerization, and a plausible mechanism for initiation was proposed. Evaluating viscoelasticity, physical properties, and adhesive performances of the produced PSAs, we demonstrated that our approach could be extensively employed to manufacture visible-light-curable PSAs with various grades. In particular, despite the poor transparency of the produced PSAs, their adhesive strength was freely adjusted from 0.40 N/cm (low enough to be used for release film in displays) to 9.90 N/cm (high enough to be used for the back film/plate in displays). However, to extend the application range of visible-light-curable PSA to OCA for displays, the amount of photocatalyst should be reduced by enhancing the efficiency of the catalytic cycle.

2. Driving the Catalytic Cycle by Additives for OCA

2.1. Strategy

In the previous section (driving the catalytic by typical monomer), despite the variable adhesive strength of the prepared PSAs, their poor transparency strictly prevent them from being applied as OCA for displays. Therefore, to produce OCA via visible-light-active photocatalyst-based polymerization, it was required to enhance the efficiency of the catalytic cycle. For this purpose, we employed an additive known to drive the catalytic cycle of the photocatalyst efficiently. The photocatalyst we used in the previous section (4DP-IPN) was used in this section, and we employed α -haloester as an additive. Since α haloesters produce radical species by dissociative electron transfer with visiblelight-active photocatalysts, they are frequently utilized as an initiator for photocatalyst-mediated atom transfer radical polymerization (Singh, et al., 2018) (**Figure 3-13a**). As in the previous section, the visible-light-curable acrylic PSAs were produced by bulk polymerization and film curing (**Figure 3-13b**), and the crosslinker (PEGDA, 0.2 wt%) was added before film curing.

a) Proposed mechanism for O-ATRP



b) Preparation of solvent-free acrylic PSAs



Figure 3-13. a) The mechanism for photocatalyst-mediated ATRP initiated by DBM (Singh, *et al.*, 2018). b) Procedure for manufacturing visible-light-curable acrylic PSAs using photocatalyst and DBM (Back, *et al.*, 2021).

In the catalytic cycle, an electron was transferred from the excited 4DP-IPN to α -haloesters; thus, α -haloesters acted as an oxidant. The oxidants should have a high reduction potential to facilitate the oxidative quenching cycle of the photocatalyst. Therefore, we expected the polymerization rate to increase when an α -haloester with a high reduction potential was employed. We tested three α -haloesters with different reduction potentials (**Figure 3-14**). All α -haloesters showed the proper ground-state reduction potentials ($E_{red}^{\circ} > -1.28$ V vs. the saturated calomel electrode (SCE)). We expected that α -haloesters we selected would drive the oxidative quenching cycle of the 4DP-IPN efficiently because they have higher reduction potentials compared to the excited-state oxidation potential of 4DP-IPN (E_{ox}^{*} , -1.28 V vs. SCE) (**Figure 3-14**).



Figure 3-14. Chemical structures and experimental/computational redox potentials of the 4DP-IPN and α -haloesters (DBM, EBiB, and EBP) (Back, *et al.*, 2021).

2.2. Preparation of Visible-Light-Curable Acrylic OCAs

2.2.1. Bulk Polymerization

Monomer compositions were set as the commonly used compositions for acrylic PSAs (or OCAs); [BA]:[IBOA]:[HBA] = 80:10:10 (Satas, 1989). As a control experiment, bulk polymerization of acrylic monomers (BA, IBOA, and HBA) was carried out using 340 ppm of UV-active PI under Ar condition (*entry 3 in* **Table 3-7**). The control experiment produced pre-polymer with a sufficient conversion (7.4%) and molecular weight (M_n, 873 kg/mol) only in 15 seconds of UV irradiation. In addition, the prepared prepolymer by the control experiment showed a proper viscosity to be coated in a film form. The negative control experiments were conducted in the absence of 4DP-IPN α -haloesters (*entry 1 in* **Table 3-7**) and 4DP-IPN (*entry 2 in* **Table 3-7**). As anticipated, no polymers were obtained without photocatalyst or α -haloesters, indicating that they were essential for initiating the photopolymerization.

It took a long irradiation time (600 s) to obtain pre-polymer with a proper conversion (11.2%) and molecular weight (418 kg/mol) excluding α -haloester (*entry 4 in* **Table 3-7**). However, as predicted, the irradiation time was significantly shortened by α -haloesters, and DBM was the most efficient oxidant than EBP and EBiB (*entries 5~8 in* **Table 3-7**). In other words, DBM with the highest reduction potential exhibited the most favorable electron transfer from the excited photocatalyst to α -haloesters, resulting in a fast polymerization rate. On the other hand, EBP with the lowest reduction potential showed a slower polymerization rate because of the relatively unfavorable photo-induced electron transfer.

Entry	α- Haloester	[M]ª:[4DP-IPN]: [α-Haloester]	Time (s)	Conversion (%)	Mn (kg/mol)	Ð
1	-	100:0:0	> 8 h	No separ	able polymer	s
2	DBM	100:0:0.1	> 8 h	No separ	rable polymer	s
3 ^a	-	100:0.034:0	15	7.42	873	1.68
4	-	100:0.005:0	600	11.2	418	2.34
5	DBM	100:0.005:0.1	10	11.7	289	2.51
6	DBM	100:0.001:0.1	10	7.68	512	2.35
7	EBP	100:0.005:0.1	180	7.76	749	1.83
8	EBiB	100:0.005:0.1	100	7.45	514	2.20

Table 3-7. Bulk polymerization results (Back, *et al.*, 2021). Mole ratio ([M]) was set as follows; [BA]:[IBOA]:[HBA] = 80:10:10. D means dispersity.

^aA photoinitiator was used instead of the 4DP-IPN.

Entry	Time (s)	Conversion (%)	M _n (kg/mol)	Ð
	> 8 h	No separ	rable polymers	
1	> 8 h	No separ	rable polymers	
	> 8 h	No separ	rable polymers	
	> 8 h	No separ	rable polymers	
2	> 8 h	No separ	rable polymers	
	> 8 h	No separ	rable polymers	
	15	7.42	873	1.68
3	15	6.21	826	1.85
	15	6.88	814	1.87
	600	11.2	418	2.34
4	500	11.3	558	2.36
	600	11.4	702	2.09
	10	11.7	289	2.51
5	10	11.4	425	2.61
	10	8.02	377	2.53
	10	10.0	255	2.52
6	10	6.14	611	2.17
0	10	8.44	530	2.66
	10	7.68	512	2.35
	180	7.76	749	1.83
7	180	9.41	1,018	1.84
	180	8.60	1,010	1.85
	100	7.45	514	2.20
8	100	7.98	938	1.89
	100	6.95	739	2.10

Table 3-8. Reproducibility results of Table 3-7 (Back, et al., 2021).

After we found that 4DP-IPN and DBM could initiate the polymerization effectively, the effect of their contents on the polymerization rate was determined. As the content of 4DP-IPN increased, the polymerization rate increased (*entries 5 and 6 in* **Table 3-7**, *entry 5 in* **Table 3-9**). Likewise, an increase in DBM contents also enhanced the polymerization rate (*entries 2-4 in* **Table 3-9**, *entries 7-9 in* **Table 3-9**).

The amount of DBM consumed during the bulk polymerization was measured using gas chromatography (**Figure 3-15**). Ethyl acetate was used as the solvent and the retention time of ethyl acetate was 7.352 min. Toluene was used as the internal standard that did not participate in the bulk polymerization, and the retention time of toluene was 15.219 min. Temperature condition for gas chromatography was set as follows; 1st step (35-130 °C, 10 °C/min), 2nd step (130-325 °C, 30 °C/min). As a result, it was found that the amount of DBM consumed during the bulk polymerization was small, and a relatively large amount of DBM remained. In particular, when the 2 ppm of 4DP-IPN was employed, only a tiny amount of DBM was consumed (0.2%).

Table 3-9. Bulk polymerization results in different content of 4DP-IPN andDBM (Back, et al., 2021). Mole ratio ([M]) was set as follows;[BA]:[IBOA]:[HBA] = 80:10:10. D means dispersity.

Entry	[M]:[4DP-IPN]:[DBM]	Time (s)	Conversion (%)	$M_n \left(kg/mol ight)$	Đ
1	100:0.005:0.05	20	13.5	369	2.19
2	100:0.005:0.05	10	4.67	304	2.52
3	100:0.005:0.5	10	18.8	189	3.04
4	100:0.005:5	10	31.9	84	2.60
5	100:0.0002:0.1	10	4.24	446	2.09
6	100:0.001:0	450	10.4	989	1.79
7	100:0.001:0.05	10	3.46	613	2.05
8	100:0.001:0.5	10	16.6	367	2.56
9	100:0.001:5	10	34.8	218	2.52

Entry	Time (s)	Conversion (%)	M _n (kg/mol)	Ð
	20*	13.5*	369*	2.19*
1	20	7.02	557	2.16
	20	10.83	477	2.50
	10*	4.67*	304*	2.52*
2	10	5.53	576	2.47
	10	5.06	536	2.59
	10*	18.8*	189*	3.04*
3	10	23.7	220	3.07
	10	17.9	226	3.15
	10*	31.9*	84*	2.60*
4	10	42.2	132	3.60
	10	41.8	136	3.30
	10*	4.24*	446*	2.09*
5	10	2.80	606	1.97
	10	2.98	680	1.78
	450	10.5	994	1.76
6	450	10.1	943	1.91
	450*	10.4*	989*	1.79*
	10*	3.46*	613*	2.05*
7	10	3.60	589	1.87
	10	3.54	523	2.04
	10	16.2	357	2.36
8	10*	16.6*	367*	2.56*
	10	18.2	392	2.53
	10*	34.8*	218*	2.52*
9	10	34.1	212	2.72
	10	36.9	205	2.90

Table 3-10. Reproducibility results of Table 3-9 (Back, et al., 2021).



4DP-IPN content	Bulk polymerization	IToluene	Idbm	IDBM/IToluene	Consumed DBM	Residual DBM
2	Before	124.98	7.43	0.059434	0.29/	00.80/
2 ppm	After	402.32	23.87	0.059331	0.270	99.870
10 ppm	Before	244.84	19.46	0.079472	Q 10/	01.09/
	After	177.55	12.97	0.073054	8.170	91.970
50	Before	153.59	12.87	0.083780	11 00/	<u>88 20/</u>
50 ppm	After	102.93	7.61	0.073891	11.070	00.270

Figure 3-15. Evaluation of remaining DBM after bulk polymerization using gas chromatography (Back, *et al.*, 2021). The content of DBM was set as 0.1 mol%.



Figure 3-16. UV/Vis spectra of the monomer mixture with 2 ppm of 4DP-IPN and 0.1 mol% of DBM (before/after bulk polymerization) (Back, *et al.*, 2021).

The UV/Vis spectra after bulk polymerization were comparable to those before, indicating that the photocatalyst was not consumed (**Figure 3-16**). The discrepancy in the yellow box in the **Figure 3-16** might be due to DBM.

Additionally, ¹H-NMR result showed that the pre-polymer was successfully manufactured (**Figure 3-17a**). The symbol x and x' mean the peaks of monomers' protons before and after bulk polymerization. **Figure 3-17b** showed the T_g of the pre-polymer, and it was confirmed that the pre-polymer exhibited a suitable T_g for use as a PSA.



Figure 3-17. Characterization of the pre-polymer obtained by bulk polymerization (*entry 6 in* **Table 3-7**); a) ¹H-NMR result and b) differential scanning calorimetry result. The left graph showed a time-temperature curve, and the right graph showed a heat flow-temperature curve (Back, *et al.*, 2021).

2.2.2. Film Curing

The film curing rate was much greater for PSAs incorporating DBM than without it (Figure 3-18a). Even with a low loading of DBM (0.1 mol%) and a 4DP-IPN (10 ppm), a very high conversion (~98%) was achieved in 5 minutes (448 nm, 0.3 mW/cm²). This conversion was equivalent to traditional UVcuring systems, which generally take about 6 minutes to cure the PSA (Baek, et al., 2017). Because of the massive quantity of remaining DBM after bulk polymerization, the film curing rate significantly increased. In addition, as shown in Figure 3-18b, we investigated the influence of the 4DP-IPN's loading on the film curing rate with a fixed content of DBM (0.1 mol%). The film curing rate was slow for 2 ppm of 4DP-IPN, but the rate significantly increased with increasing 4DP-IPN content. There was no significant difference in the film curing rate when the photocatalyst content was 10 and 50 ppm. Therefore, we established that the optimal content of DBM and 4DP-IPN was 0.1 mol% and 10 ppm, respectively, based on the results of both bulk polymerization and film curing. As a result, even at a low photocatalyst content (10 ppm), we determined that adding a tiny quantity of DBM increased the photocatalystbased photopolymerization rate by more than six times; film curing time to accomplish saturated conversion fell from 60 to 10 minutes.



Figure 3-18. Conversion of the film curing as a function of irradiation time: a) 4-DP-IPN was set as 50 ppm, and b) DBM was set as 0.1 mol% (Back, *et al.*, 2021).

2.3. Characterization of Visible-Light-Curable Acrylic OCAs

2.3.1. Gel Content

Next, we investigated the gel content of the prepared PSAs with different content of DBM and 4DP-IPN (Figure 3-19). As the amount of DBM increased with the fixed 4DP-IPN content, the gel cont sharply decreased. This result might be ascribed to the sharp decrease in molecular weight. With the high amount of DBM (5 mol%), the pre-polymer showed low molecular weight (84~218 kg/mol, Table 3-9) because of a high concentration of the initiating group. In addition, it was confirmed that the molecular weight was still low even after the film curing (Figure 3-20). After the film curing, the minor peak was detected in the high molecular weight region, but the peak of the SEC curve (M_p) shifted to the low molecular weight region (from 123 kg/mol to 89 kg/mol). The ratio of shifting to the left decreased, and M_p was much lowered (47 kg/mol) even without the crosslinker. These results might be caused by the large amount of remaining DBM (92.1%) after bulk polymerization. The excess of initiating group in the film curing step led to a sharp decrease in the molecular weight; thus, PSA's crosslinking density was drastically reduced (Zhao, et al., 2013, Zhao, et al., 2015). On the other hand, when the optimal DBM content was employed (0.1 mol%), the prepared PSA showed a sufficiently high gel content (> 78%). This result indicated that the polymer chains were successfully crosslinked; thus, the prepared PSAs were expected to exhibit high cohesive strength (Benedek, et al., 1997).



Figure 3-19. The gel content of the prepared PSAs with different a) DBM and b) 4DP-IPN content. The curing time was fixed as 30 min (Back, *et al.*, 2021).



Before	392.90	1321.57	3.363672	7.004	02 104
After	153.19	474.46	3.097233	1.9%	92.1%

Figure 3-20. a) M_p (molecular weight at the peak of the curve) obtained from SEC curve and b) remaining DBM obtained from gas chromatography (Back, *et al.*, 2021).

2.3.2. Transparency

One of the essential requirements of OCA for displays was optical transparency, and we assessed it using UV/Vis spectroscopy (Figure 3-21a). Since the visible-light-active photocatalyst strongly absorbs the visible-light region, the optical transparency of visible-light-curable PSA is strictly affected by the content of the photocatalyst. Therefore, the transmittance at 400 nm increased from 92.4 to approximately 100%, as the amount of photocatalyst decreased from 50 to 2 ppm. The transmittance of PSA with 10 ppm of 4DP-IPN was similar to that with 50 ppm of 4DP-IPN. Thus, the prepared PSAs with 10 or 50 ppm of 4DP-IPN showed excellent transparency comparable to conventional OCAs (99%, 3MTM OCAs 8211, 8212, 8213, 8214, and 8215). We additionally manufactured acrylic OCA via conventional UV-curing (UV dose: 3 J/cm²) as follows; pre-polymer was obtained by UV-induced bulk polymerization (entry 3 in Table 3-7), and the film curing was conducted after adding a crosslinker (0.2 wt%, PEGDA) and PI (0.3 wt%, Irgacure 184). As presented in Figure 3-22, the prepared acrylic PSA showed excellent transparency in the visible-light region; transmittance at 400 nm was approximately 98%. This result also supported that the prepared visible-lightcurable acrylic PSAs showed the same level of transparency as the conventional acrylic OCA.





Figure 3-21. a) Structure of the test specimens for evaluating transparency and pictures of the specimens. b) UV/Vis spectra of the prepared PSAs with different 4DP-IPN content (Back, *et al.*, 2021). DBM content was fixed as 0.1 mol%. The irradiation time was set as 30 min for all specimens except for the PSA with 2 ppm of 4DP-IPN (irradiation time: 2 h).



Figure 3-22. UV/Vis spectra of traditional UV-curable acrylic PSA (Back, *et al.*, 2021).

2.3.2. Physical Properties and Adhesive Performances

The physical property of the prepared visible-light-curable PSAs was assessed by the single lap shear test (**Figure 3-23**). The lap shear strength values of the prepared visible-light-curable acrylic PSAs did not differ significantly (~ 0.3 MPa), and these values were equivalent to those of previously reported values for photo-responsive acrylic PSAs ($0.15\sim0.34$ MPa) (Harper, *et al.*, 2017, Kim and Chung, 2017).



Figure 3-23. Example strain-stress curve for the single lap shear test and the obtained lap shear strength of the prepared PSAs (Back, *et al.*, 2021).

The prepared PSAs' adhesive performances, i.e., peel strength, loop tack, and holding time, were examined to determine whether they could be employed as traditional acrylic OCAs. The peel strength and loop tack of the produced PSAs declined as the DBM content increased at a fixed 4DP-IPN (50 ppm), whereas the holding time was continuously reduced (Figure 3-24a). This trend might be related to a drop in PSA's gel content since low gel content increased wetting ability but lowered the cohesive strength (Benedek and Heymans, 1997). The considerable drop in the M_n of the PSA might explain the dramatic decline in the adhesive performances of the PSA with 5 mol% of DBM. Actually, these results were not matched with the results of lap shear strength because testing conditions of holding time were different from the single lap shear test. Lap shear strength denotes resistance to fracture, but holding time denotes resistance to creep deformation. In addition, although the single lap shear test was conducted at an ambient temperature (25°C), the holding test was conducted at an elevated temperature (50°C). The holding time of the produced PSA was considerably extended when the content of 4DP-IPN was reduced from 50 to 10 ppm (Figure 3-24b). However, the peel strength and loop tack remained similar. These results might be caused by a slight rise in PSA's gel content with decreasing 4DP-IPN content.



Figure 3-24. Peel strength, loop tack, and holding time of the prepared PSAs with different a) DBM content (4DP-IPN: 50 ppm) and b) 4DP-IPN content (DBM: 0.1 mol%). The curing time was fixed as 30 minutes (Back, *et al.*, 2021).

The produced PSAs' peel strength (2.8~8.0 N/cm) and loop tack (4.1~8.2 N/cm) showed that they might be employed as traditional acrylic OCAs (Baek and Hwang, 2017, Beharaj, *et al.*, 2019, Park, *et al.*, 2015, Sulley, *et al.*, 2020). In particular, the PSA containing 0.1 mol% of DBM and 10 ppm of 4DP-IPN showed superior shear resistance (higher than 100 h of holding time) and transparency (approximately 100% of transmittance at 400 nm). These results indicated that the produced PSAs exhibited excellent performances to be used as OCA for displays. Finally, the overall results (polymerization behavior and adhesive performances) indicated that 0.1 mol% of DBM and 10 ppm of 4DP-IPN were the best conditions for producing visible-light-curable acrylic OCA.

2.4. Conclusions

In this section, visible-light-active photocatalyst-based photopolymerization was facilitated by employing α -haloester to manufacture the OCA for displays. Even with the small amount of 4DP-IPN (10 ppm), the polymerization rate was significantly enhanced by adding α -haloester; thus, the rate of the developed visible-light-curing was comparable to traditional UV-curable acrylic PSAs. The highest efficiency of the catalytic cycle was achieved when DBM, the highest reduction potential among α -haloesters, was used. In other words, the content of 4DP-IPN could be drastically lowered to 10 ppm by using DBM; thus, the transparency of the PSA could increase to a similar level of OCA for displays (approximately 100% at 400 nm). However, it should be noted that a large amount of DBM remains after bulk polymerization, and the remaining halogen-based additives generally cause severe problems. Additionally, the polymerization condition was strictly limited to the oxygen-free condition because of poor oxygen tolerance of oxidative quenching cycles. Therefore, to further improve the photocatalyst-based visible-light-curing system, the reductive quenching cycle should be employed instead of the oxidative quenching cycle, and halogen-based additives should be excluded in the following work.

3. Optimization of the Catalytic Cycle with Various Photocatalysts and Additives for UV-blocking OCA

3.1. Strategy

3.1.1. Designing photocatalysts and Reductants

In the previous section (driving the catalytic cycle by additives), we successfully manufactured visible-light-curable OCA with a low photocatalyst loading. However, there were several limitations; oxygen sensitivity and the use of the halogen-based additive. Therefore, visible-light-induced photopolymerization was driven by the reductive quenching cycle using amine-based additives to address these issues.

Tertiary amines may be the best sacrificial reductants since they can also act as an initiator and oxygen scavengers. Photo-induced electron transfer from tertiary amine to the excited photocatalyst generates amine radical cation (R₃N⁺⁺), which loses a proton to form α -amino radical species. The generated α -amino radical species act as an initiator of the polymerization (Ligon, et al., 2014). Tertiary amines can also reduce oxygen inhibition by converting unreactive peroxyl radicals to reactive species, *i.e.*, α -amino radical species (Hayyan, et al., 2016, Islam, et al., 2008). In addition, the ground-state photocatalyst can be regenerated by an electron transfer between photocatalyst radical anion and oxygen (Hari, et al., 2011, Rueping, et al., 2011). We employed four sacrificial reductants with different HOMO levels to optimize the reductive quenching cycle of photocatalyst.

To generate long-lived T₁, a visible-light-active photocatalyst with a strongly twisted donor-acceptor structure was employed because such a photocatalyst usually satisfies the requirements; a small energy gap and the orthogonality rule (Singh, et al., 2018). In addition to the previously studied photocatalyst (4DP-IPN), we employed three additional photocatalysts with different HOMO levels. Since the electron transfer from photocatalyst to reductant is usually located in the Marcus "normal region", photo-induced electron transfer rate increased with decreasing HOMO level of photocatalyst (Silverstein, 2012). Therefore, we adjusted the HOMO level of photocatalyst by employing an electronwithdrawing group (-CN) in the donor group (Figure 3-25).). A full description of the synthesis and characterization of the photocatalysts (i.e., ¹H-NMR spectra, UV/Vis absorption spectra, PL emission spectra, and cyclic voltammograms) are provided in the reference (Back, et al., 2022). We expected that the photocatalyst with the lowest HOMO level and the reductant with the highest HOMO level would be the best combination for the reductive quenching cycle (red boxes in Figure 3-25).


Figure 3-25. Chemical structures of photocatalysts and sacrificial reductants with different HOMO levels (Back, *et al.*, 2022).

3.1.2. Hybrid Reductant

As mentioned in *Chapter 1 "Introduction"*, the final purpose of this section is manufacturing UV-blocking OCAs for foldable displays. The OCA for foldable displays should dissipate the folding/unfolding-induced stress to prevent delamination and/or warping of the stacked layers (Campbell, et al., 2017, Lee, et al., 2019). Since 2016, research on PSA/OCA for foldable displays has been in progress, and many studies have been conducted to control strain recovery and stress relaxation (Table 3-11). The crosslinking degree could control these two properties; when the crosslinking degree increases, strain recovery increases, but stress relaxation decreases (Lee, et al., 2017). Conventionally, the crosslinking degree is adjusted by the content of crosslinking agents such as PEGDA. However, we employed the hybrid reductant using both an additive-type reductant (DMAEAc) and a monomertype reductant (DMAEA) to minimize the use of the additive-type reductant (Figure 3-26). Two reductants have a similar structure; there is no significant difference in polymerization rate. Since the additive-type reductant (DMAEAc) produced the linear polymer, we expected that crosslinking degree would decrease when the portion of the DMAEAc increased. On the other hand, the monomer-type reductant (DMAEA) induced the crosslinking of the polymer; thus, the crosslinking degree would increase when the portion of the DMAEA increased. The hybrid reductant was employed at the bulk polymerization step, and in the film curing step, no additives were added except for the UV absorber.

Doforonoo		(Lee, <i>et</i> al., 2016)	(Behling, <i>et al.</i> , 2016)	(Lee, <i>et</i> <i>al.</i> , 2017)	(Lee, <i>et</i> al., 2017)	(Lee, <i>et</i> al., 2019)	(Back, et al., 2019)	(Lee, <i>et</i> al., 2019)	(Lee, <i>et</i> <i>al.</i> , 2019)	(Park, <i>et</i> al., 2020)	(Lee, <i>et</i> <i>al.</i> , 2021)
Stress	relaxation (%)	~ 70% ^{a)} (Strain: 400%)	42% (Strain: 900%)	~ 50% ^{a)} (Strain: 400%)	ı	~ 79% ^{a)} (Strain: 500%)	70.6% (Strain: 300%)	ı	~ 85% ^{a)} (Strain: 400%)	18% ^{a)} (Strain: 10%)	47.8% (Strain: 300%)
Strain	recovery (%)	~93% ^{a)} (Strain: 400%)	99% ^{b)} (Stress: 95kPa)	~ 97% ^{a)} (Strain: 400%)	~ 92% ^{a)} (Strain: 500%)	~ 94% ^{a)} (Strain: 500%)	71.2% (Strain: 300%)	ı	~ 90% ^{a)} (Strain: 400%)	77% (Strain: 10%)	I
Dool strongth		~ 6 N/cm ^{a)} (Steel)	1.5 N/cm (Polyester)	~ 6 N/cm ^{a)} (Steel)	~ 3.8 N/cm ^{a)} (Steel)	~ 10 N/cm ^{a)} (Steel)		~ 0.8 N/cm ^{a)} (Steel)	$\sim 5.5 \text{ N/cm}^{a}$ (Steel)	~ 8 N/cm ^{a)} (Polyacrylate)	~ 5.6 N/cm ^{a)} (Steel)
Gel	content	~ 70% ^{a)}	I	~ 75% ^{a)}	I	I	ı	I	I	ı	%66
Dronouotion	r iepai auon	Solvent & Thermal curing	UV curing	Solvent & Thermal curing	Solvent & Thermal curing	Solvent & Thermal curing	UV curing (patterning)	Solvent & UV curing	Solvent & Thermal curing	UV curing	UV curing
tion	Additive	PIR	HDDA	PIR	Pt	PIR, SIS	PEGDMA	HDDA, silica	PIR, AE	DSN	HDDA, silica
Composi	Polymer	EHA, BA, EA, HEMA, AA	EHA, HBA	EHA, IBOA, GMA, HEA	PDMS ^{c)}	EHA, HEMA, BA, AA	EHA, IBOA, AA, MMA, HEA	EHA, MA	Polyacrylate ^{d)}	BA, EHA, MMA, AA	EHA, AA
Tntru -	tuu y	-1	5	${\mathfrak m}$	4	S	9	Ζ	8	6	10

Table 3-11 (1). References for PSAs/OCAs for flexible/stretchable displays (Back, et al., 2022).

Folyaciyiate EHA, IBOA, AA, MMA, HEA HEA BA, IBOA, NVC BA, HEA	Additive PEGDA PEGDMA PEGDMA β-CD-AOI	Preparation UV curing UV curing UV curing (patterning) UV curing	Gel content 45% 94%	Peelstrength $\sim 0.3 \mathrm{N/cm^{ab}}$ $\sim 0.3 \mathrm{N/cm^{ab}}$ (Steel)6.2 $\mathrm{N/cm}$ (Steel)10 $\mathrm{N/cm}^{ab}$ $\sim 8.5 \mathrm{N/cm^{ab}}$	Strain recovery (%) $\sim 80\%^{a)}$ (Strain: 50%) > 90% (Strain: 300%) $\sim 87\%^{a)}$ (Strain: 300%) $\sim 77\%$ (Strain: 100%) $\sim 80\%^{a)}$	Stress relaxation (%) ~ 45% ^{a)} (Strain: 50%) 78% (Strain: 100%) ~ 15% ^{a)}	Reference (Kim, et al., 2021) (Kim, et al., 2021) (Yi, et al., 2021) (Yi, et al., 2021) (Park et al.)
Polyacrylate ^{d)} EHA, HEA BA, MMA, AA EEA, HEA EHA, CEA	EN USLA PETA edition	UV curing UV curing UV curing UV curing	~ 60% ^{a)} ~ 5% ^{a)} 82%	(Polyacrylat e) ~ 3.5 N/cm ^{a)} (Polyacrylat e) ~ 9.1 N/cm ^{a)} (Unknown) 2.3 N/cm (Polyimide) ~ 10 N/cm ^{a)}	~ 50.0% (Strain: 10%) 69% (Strain: 400%) ~ 70% ^{a)} (Strain: 10%) 42%	 C1.5% (Strain: 10%) 98% (Strain: 400%) ~ 10%^a) (Strain: 10%) 93% (Strain: 400%) 42.1% 	(TatX, et al., 2021) (Seok, et al., 2022) (Kim, et al., 2022) (Seok, et al., 2022) (Lim, et al., 2022)

Table 3-11 (2). References for PSAs/OCAs for flexible/stretchable displays (Back, et al., 2022).



Figure 3-26. Illustration for the hybrid reductant using DMAEAc and DMAEA (Back, *et al.*, 2022).

3.1.3. Monomer Composition

We employed acrylic monomers (BA and HBA) that are known to yield flexible OCAs proper for foldable displays (Behling, et al., 2016). Since OCAs for foldable displays should exhibit excellent flexibility even at a low temperature, high content of low T_g monomer, i.e., BA, is required. Furthermore, HBA can increase the cohesive strength through hydrogen bonding without significantly changing the T_g of the PSA. We additionally conducted a pre-test to decide the monomer composition for OCA as follows (**Table 3-12**); 10 ppm of 4Cz-IPN and 0.5 mol% of DMAEAc were used as photocatalyst and reductant, respectively. Bulk polymerization was conducted under air conditions, and the film curing time was 10 minutes. As the amount of HBA increased, the peel strength was significantly enhanced because of the increase in the cohesive strength. Therefore, we employed the monomer composition; [BA]:[HBA] = 80:20.

 Table 3-12. Peel strength of the prepared PSAs with different monomer compositions (Back, *et al.*, 2022).

Entry	[BA]:[HBA]	Adherend	Peel strength (N/cm)
1	100:0	Glass	1.18 (±0.11)
2	90:10	Glass	4.44 (±0.21)
3	80:20	Glass	8.64 (±0.34)
4	100:0	CPI	0.82 (±0.02)
5	90:10	CPI	4.02 (±0.32)
6	80:20	CPI	8.39 (±0.77)

3.2. Preparation of Visible-Light-Curable Acrylic OCAs

3.2.1. Bulk Polymerization

As a negative control experiment, bulk polymerization was conducted using photocatalyst or reductant alone (**Table 3-13**). Polymerization was possible using 4DP-IPN or 4Cz-IPN alone, whereas polymerization was impossible when only a reductant was used. UV-induced bulk polymerization was successfully achieved using 1000 ppm of UV-active PI; the pre-polymer was obtained with a suitable molecular weight (1,207 kg/mol) and conversion (5.04%) only in 20 s of irradiation time. However, all entries could not be polymerized under air conditions, indicating the oxygen sensitivity of the free radical polymerization.

When the photocatalyst and reductant were used simultaneously, most entries were successfully polymerized, but the result differed from expected (**Table 3-14**). We expected that the 4-*p*,*p*-DCDP-IPN/DIPEA would be the best combination, but the 4Cz-IPN/DMAEAc was the best for the following four reasons. First, despite the oxygen-acceleration behavior of 4-*p*,*p*-DCDP-IPN, it showed poor solubility to acryl monomers (**Figure 3-27**); thus, it could not be used for OCA. Second, 4-*o*,*p*-DCDP-IPN generated less triplet, which caused poor polymerization behavior. Third, photo-induced electron transfer rate from the reductant to the excited photocatalyst was slow for 4DP-IPN. Fourth, DMAEAc showed the most excellent generation of α -amino radical species, indicating the most efficient initiation of the polymerization. The coworker (Younghwan Kwon and Prof. Minsang Kwon) supported evaluating the photocatalyst's triplet generation/ photo-induced electron transfer rate and reductant's α -amino radical generation (Back, *et al.*, 2022).

Entry	Photocatalyst/PI	Reductant	Atm.	Conversion (%)	Mn (kg/mol)	Ð
1 ^a	-	DMAEAc	Argon	0	-	-
2ª	-	DMAEAc	Air	0	-	-
3 ^b	4DP-IPN	-	Argon	0.89	380	1.40
4 ^b	4DP-IPN	-	Air	0	-	-
5 ^b	4Cz-IPN	-	Argon	3.82	385	1.42
6 ^b	4Cz-IPN	-	Air	0	-	-
7 ^b	4-o,p-DCDP-IPN	-	Argon	0	-	-
8 ^b	4-o,p-DCDP-IPN	-	Air	0	-	-
9 ^b	4- <i>p</i> , <i>p</i> -DCDP-IPN	-	Argon	0	-	-
10 ^b	4- <i>p</i> , <i>p</i> -DCDP-IPN	-	Air	0	-	-
11°	-	-	Argon	0	-	-
12°	-	-	Air	0	-	-
13°	Irgacure 184	DMAEAc	Argon	5.04	1,207	1.16
14°	Irgacure 184	DMAEAc	Air	0	-	-

Table 3-13. Bulk polymerization results of negative control experiments (Back,*et al.*, 2022).

^aReductant content: 0.5000 mol%, irradiation time: 30 s.

^bPhotocatalyst content: 10 ppm, irradiation time: 30 s.

°PI content: 1000 ppm, irradiation time: 20 s (365 nm, 1 mW/cm²).

Entry	Photocatalyst	Reductant	Atm.	Conversion (%)	Mn (kg/mol)	Ð
1	4DP-IPN	DMAEAc	Argon	6.7	550	1.28
2	4DP-IPN	DMAEAc	Air	No sep	arable polymer	•
3	4Cz-IPN	DMAEAc	Argon	20.0	177	1.47
4	4Cz-IPN	DMAEAc	Air	23.0	264	1.57
5	4-o,p-DCDP-IPN	DMAEAc	Argon	1.3	695	1.23
6	4-o,p-DCDP-IPN	DMAEAc	Air	No sep	arable polymer	•
7	4-p,p-DCDP-IPN	DMAEAc	Argon	6.1	24	1.94
8	4- <i>p</i> , <i>p</i> -DCDP-IPN	DMAEAc	Air	24.0	112	1.74
9	4Cz-IPN	-	Argon	3.8	385	1.42
10	4Cz-IPN	-	Air	No sep	arable polymer	•
11	4Cz-IPN	DIPEA	Argon	4.0	390	1.32
12	4Cz-IPN	DIPEA	Air	No sep	arable polymer	•
13	4Cz-IPN	TEA	Argon	18.8	201	1.47
14	4Cz-IPN	TEA	Air	14.8	289	1.41
15	4Cz-IPN	DMBA	Argon	11.2	90	1.58
16	4Cz-IPN	DMBA	Air	15.7	206	1.46

Table 3-14. Bulk polymerization results with various photocatalysts andreductants (Back, *et al.*, 2022). Irradiation time was set as 30 s.

Table 3-15. Reproducibility results of Table 3-14 (*entries 1~8*) (Back, *et al.*,2022).

Entry	Photocatalyst	Reductant	Atm.	Conversion (%)	Mn (kg/mol)	Ð
				6.71	550	1.28
1	4DP-IPN	DMAEAc	Argon	5.68 5.87	576 594	1.33 1.29
				20.01	177	1.47
2	4Cz-IPN	DMAEAc	Argon	17.72 17.54	200 201	1.47 1.49
				1.32	695	1.23
3	4-o,p-DCDP-IPN	DMAEAc	Argon	0.88 0.82	642 629	1.36 1.39
				6.12	24	1.94
4	4- <i>p,p</i> -DCDP-IPN	DMAEAc	Argon	6.30 5.95	21 19	1.90 2.04
	4DP-IPN		Air	0	-	-
5		DMAEAc		0 0	-	-
			Air	22.99	264	1.57
6	4Cz-IPN	DMAEAc		18.8 18.92	304 294	1.39 1.45
				0	-	-
7	4- <i>o,p</i> -DCDP-IPN	DMAEAc	Air	0 0	-	-
				23.97	112	1.74
8	4- <i>p,p</i> -DCDP-IPN	DMAEAc	Air	25.25 23.10	106 130	1.77 1.57

Entry	Photocatalyst	Reductant	Atm.	Conversion (%)	M _n (kg/mol)	Đ
				11.2	90	1.58
1	4Cz-IPN	DMBA	Argon	10 9.92	89 110	1.78 1.57
				20.01	177	1.47
2	4Cz-IPN	DMAEAc	Argon	17.72 17.54	200 201	1.47 1.49
				18.83	201	1.47
3	4Cz-IPN	TEA	Argon	16.31 16.99	237 237	1.45 1.46
				4.02	390	1.32
4	4Cz-IPN	DIPEA	Argon	4.02 3.78	480 503	1.32 1.28
				15.74	206	1.46
5	4Cz-IPN	DMBA	Air	14 13.22	198 210	1.58 1.57
				22.99	264	1.57
6	4Cz-IPN	DMAEAc	Air	18.8 18.92	304 294	1.39 1.45
				14.75	289	1.41
7	4Cz-IPN	TEA	Air	12.12 11.95	291 301	1.43 1.38
				0	-	-
8	4Cz-IPN	DIPEA	Air	0 0	-	-

Table 3-16. Reproducibility results of Table 3-14 (*entries 9~16*) (Back, *et al.*,2022).



Figure 3-27. Photographs of monomer mixtures with 10 ppm of photocatalyst (Back, *et al.*, 2022).

The bulk polymerization was also conducted using different content of DMAEAc (**Table 3-17**) and 4Cz-IPN (**Table 3-18**). It was confirmed that the polymerization rate was enhanced when the amount of 4Cz-IPN or DMAEAc increased. The optimal content of DMAEAc was 0.5 mol%, and the polymerization rate did not increase even when the DMAEAc content was higher than the optimum. In addition, when 10 ppm of 4Cz-IPN was employed, the polymerization rate was sufficiently fast, and the molecular weight was the smallest of other entries with different 4Cz-IPN loadings, indicating the highly efficient initiation. These results supported that the combination of 4Cz-IPN/DMAEAc effectively initiated bulk polymerization, and their optimal contents were 10 ppm and 0.5 mol%, respectively.

Table 3-17. Bulk polymerization results in different DMAEAc content (Back, *et al.*, 2022). 4Cz-IPN content and irradiation time were set as 10 ppm and 30 s, respectively.

Entry	DMAEAc (mol%)	Atm.	Conversion (%)	M _n (kg/mol)	Ð
1	0	Argon	3.82	385	1.42
2	0.1	Argon	8.77	161	1.55
3	0.3	Argon	18.46	172	1.51
4	0.5	Argon	20.01	177	1.47
5	1	Argon	19.23	193	1.45
6	0	Air	0	-	-
7	0.1	Air	0	-	-
8	0.3	Air	19.81	273	1.58
9	0.5	Air	22.99	264	1.57
10	1	Air	22.23	303	1.48

Table 3-18. Bulk polymerization results in different 4Cz-IPN content (Back, *et al.*, 2022). DMAEAc content and irradiation time were set as 0.5 mol% and 30 s, respectively. Bulk polymerization was conducted under air conditions.

Entry	4Cz-IPN (ppm)	Conversion (%)	M _n (kg/mol)	Đ
1	5	13.73	320	1.48
2	10	20.01	177	1.47
3	20	24.88	264	1.42

From the above bulk polymerization results, we found that the developed visible-light-photocatalyst-based polymerization showed excellent polymerization behavior even under air conditions, indicating strong oxygen tolerance. The reason why oxygen tolerance is important in free radical polymerization is as follows; the degassing process can be excluded from bulk polymerization when oxygen tolerance is granted. Therefore, by granting oxygen tolerance, the production rate can be increased, and the cost can be reduced. The critical process for oxygen tolerance is converting inactive peroxy radicals to active radical species by hydrogen abstraction. Therefore, the bond dissociation energy (BDE) of C-H at the α -position of tertiary amine should be lower to improve oxygen tolerance. From the BDE calculated by the coworker, the BDE of DMAEAc was lower than DIPEA, supporting the results that DMAEAc showed strong oxygen tolerance (Back, et al., 2022). Based on the bulk polymerization results, a plausible mechanism for the catalytic cycle of 4Cz-IPN and the initiation process of DMAEAc was proposed (Figure 3-28).



Figure 3-28. The proposed mechanism for visible-light-photocatalyst-based polymerization uses sacrificial reductants (Back, *et al.*, 2022).

Table 3-19. Bulk polymerization results in different visible-light-active photocatalyst-based systems (Back, *et al.*, 2022). The contents of photocatalyst and PI were set as 10 and 1000 ppm, respectively.



Entry	Photocatalyst/PI	Atm.	Conversion (%)	Mn (kg/mol)	Ð
1 ^a	4DP-IPN	Air	0	-	-
2ª	4DP-IPN	Argon	23.89	425	1.40
3ª	4Cz-IPN	Air	0	-	-
4 ^a	4Cz-IPN	Argon	3.79	366	1.40
5	4DP-IPN	Air	0	-	-
6	4DP-IPN	Argon	15.48	533	1.08
7	4Cz-IPN	Air	0	-	-
8	4Cz-IPN	Argon	2.84	441	1.12
9 ^b	Irgacure 184	Air	0	-	-
10 ^b	Irgacure 184	Argon	5.22	1319	1.13

^aIrradiation time: 30 s, DBM content: 0.1 mol%.

^bIrradiation time: 300 s, NVP was used instead of HBA.

^cIrradiation time: 20 s (365 nm, 1 mW/cm²).

After optimizing the photocatalyst/reductant, we compared the best combination (4Cz-IPN/DMAEAc) with others previously studied in this paper (**Table 3-19**). As a result, under argon conditions, it was confirmed that the polymerization rate using the optimized combination was much higher than 4DP-IPN/NVP and similar to 4DP-IPN DBM. In addition, including traditional UV-active PI-based curing, *all entries in* **Table 3-19** could not be polymerized under air conditions. However, the optimized combination facilitated polymerization even under air conditions.

Additionally, before we employed DMAEA for a hybrid reductant, we confirmed whether DMAEA crosslinked the pre-polymer during the bulk polymerization (**Table 3-20**). As a result, the gel content rose as irradiation time increased. However, the gel did not form at the conditions we utilized (30 s).

Table 3-20. Conversion and gel contents as a function of irradiation time (Back, *et al.*, 2022). The contents of 4Cz-IPN and DMAEA were set as 10 ppm and 0.5 mol%, respectively.

Entry	Irradiation time (s)	Conversion (%)	Gel content (%)
1	30	23.0	0.2
2	60	37.0	1.5
3	180	48.2	5.4

3.2.2. Film Curing

After the bulk polymerization was conducted under air conditions, the obtained pre-polymer was cured in a film form. Although the film curing rate was improved with increasing DMAEAc content, there was no significant difference between 0.5 and 1 mol% of DMAEAc (Figure 3-29a). In other words, the optimal content of DMAEAc was 0.5 mol%, the same as the optimum already determined by the bulk polymerization results. We also determined the effect of reductant type on the film curing rate (Figure 3-29b). It was found that DMAEAc and TEA exhibited excellent curing rates comparable to traditional UV-curing systems with UV blacklight. (Figure 3-7). However, since TEA is so volatile that it can cause severe problems with the reliability of products, we selected DMAEAc as the best reductant. In addition to DMAEAc, we employed monomer-type reductants structurally similar to DMAEAc but with other reactive groups such as acrylate (DMAEA) or methacrylate (DMAEMA). As a result, DMAEA showed a similar curing rate to DMAEAc, while DMAEMA showed the slowest curing rate because of the slower propagation rate of the methacrylate group. Therefore, DMAEA, rather than DMAEMA, was used as a monomer-type reductant that increased the crosslinking degree in the hybrid reductant.



Figure 3-29. Film curing conversion with a) different DMAEAc contents and b) reductant types. The content of 4Cz-IPN was fixed as 10 ppm (Back, *et al.*, 2022).



Figure 3-30. Film curing conversion with different 4Cz-IPN content. The content DMAEAc was fixed as 0.5 mol% (Back, *et al.*, 2022).

Additionally, we assessed the film curing rate using different 4Cz-IPN content (**Figure 3-30**). The polymerization rate was improved with increasing 4Cz-IPN content, but there was no significant difference between 4Cz-IPN 10 and 20 ppm. These results indicated that the optimal content of 4Cz-IPN was 10 ppm, the same as the optimum determined by the bulk polymerization.

3.3. Characterization of Visible-Light-Curable Acrylic OCAs

3.3.1. Physical Properties and Adhesive Performances

Before evaluating the physical properties of the produced PSAs, we evaluated whether they were transparent enough to be used as OCA through UV/Vis spectroscopy (**Figure 3-31**). As expected, transparency improved as the photocatalyst content decreased, and there was no significant difference in transparency between 10 and 20 ppm of 4Cz-IPN (approximately 100% of transmittance at 400 nm). These results supported that the optimal content of 4Cz-IPN was 10 ppm, and the prepared PSAs could be utilized as OCAs.





Figure 3-31. a) UV/Vis spectra of the prepared visible-light-curable OCA. b) photographs of the pre-polymer (left) and the cured OCA (right). The content of DMAEAc was fixed as 0.5 mol% (Back, *et al.*, 2022).

After that, we evaluated the gel content of the prepared OCAs to compare the crosslinking degree (**Table 3-21**). Even without using PEGDA, a relatively high gel content (44.4%) was obtained. As a result of additional experiments to find the cause of unintended crosslinking, it was confirmed that the gel content increased as the HBA content increased (*entries* $1 \sim 3$ in **Table 3-21**). These results were the same in the visible-light-active photocatalyst and the UV-active PI systems (*entries* $1 \approx 3 * in$ **Table 3-21**). This unexpected crosslinking might be caused by a hydrogen abstract from HBA incorporated in a polymer backbone (**Figure 3-32a**). More extensive research to understand the crosslinking mechanism has not been further investigated.

A certain level of gel content could be achieved without PEGDA, but the crosslinking degree had to be further increased to apply the prepared OCAs to foldable OCAs. Therefore, the ratio of DMAEA was increased, and the gel content could be increased accordingly (*entries 3~8 in* **Table 3-21**). The crosslinking mechanism by DMAEA (or DMAEMA) was predicted as follows (**Figure 3-32b**); the iminium ion could be generated as an intermediate in the catalysis of the photocatalyst. After that, the reaction between the iminium ion and HBA could form the bifunctional species, causing the polymer's crosslinking. Additionally, we assessed the gel content of the commercially available foldable OCA (CEF 3602, 3M). The gel content of the commercial foldable OCA was 64.0%, similar to the gel contents of *entries 5 and 6* in **Table 3-21**.

T-4	Reductant	Monomer	Bulk p	olymerization		Cured film
Ent ry	[DMAEAc] :[DMAEA]	[BA] :[HBA]	Conversion (%)	Mn (kg/mol)	Đ	Gel content (%)
1^{a}	100:0	100:0	26.01	277	1.31	~ 0
1* ^b	100:0	100:0	4.63	1,194	1.15	~ 0
2 ^a	100:0	90:10	28.72	258	1.38	~ 0
2* ^b	100:0	90:10	3.57	1,350	1.13	6.6 (±3.9)
3 ^a	100:0	80:20	21.8	344	1.33	44.4 (±3.1)
3* ^b	100:0	80:20	3.26	1,386	1.13	80.6 (±4.7)
4 ^a	80:20	80:20	20.04	340	1.38	55.1 (±3.3)
5 ^a	60:40	80:20	20.74	332	1.41	68.6 (±4.8)
6 ^a	40:60	80:20	18.59	346	1.42	76.0 (±1.3)
7 ^a	20:80	80:20	17.11	388	1.35	78.5 (±2.8)
8 ^a	0:100	80:20	20.83	363	1.38	82.1 (±1.3)
9°		3M F	oldable OCA			64.0 (±1.1)

Table 3-21. Bulk polymerization and gel content results in different monomer/hybrid reductant compositions (Back, *et al.*, 2022). The film curing time and reductant content were set as 10 min, 0.5 mol%, respectively.

^a4Cz-IPN content: 10 ppm, bulk polymerization (air).

^bPI (Irgacure 184) content: 1000 ppm, bulk polymerization (argon, 1 mW/cm², 20 s), film curing (6 mW/cm², 10 min).

°Commercial product of foldable OCA (CEF 3602, 3M, thickness: 50 µm).

a) Possible pathway 1



b) Possible pathway 2



Figure 3-32. Proposed mechanism for crosslinking by a) HBA and b) DMAEA or DMAEMA (Back, *et al.*, 2022).

We next investigated the peel strength of the prepared OCAs employing a different ratio of the hybrid reductant (Table 3-22). Since CPI film or ultra-thin glass has been used for the cover window in foldable displays, we employed CPI and glass as the substrate for the peel test. When the proportion of DMAEA increased, the peel strength decreased because the high crosslinking degree reduced PSA's wettability (Tobing and Klein, 2001). Most PSAs, including commercial foldable OCAs, generally show superior adhesive strength to the hydrophilic substrate rather than the hydrophobic substrate because of the differences in wetting (Kowalski and Czech, 2015). On the other hand, the produced OCAs had significantly greater peel strength to CPI than to glass, which is unusual in traditional PSAs. Remarkably, the peel strength of the produced OCAs with specific compositions (DMAEA 40 or 60%) was three times higher than commercial foldable OCA (substrate: CPI). To understand this unusual trend, we further evaluated the peel strength according to the attachment time (Figure 3-33). When the CPI was used as the substrate, the peel strength of the produced OCA was low at the beginning of attachment, but it was dramatically enhanced as attachment time increased. Although the peel strength increases with increasing attachment time because of PSA's wettability (Girard-Reydet, et al., 2004), such a steep increase is not typical. We speculated that this unusual increase in the peel strength might be due to an unexpected interaction between the prepared OCA and CPI (such as hydrogen bonding and electron donor-acceptor), but the exact cause is still unknown.

Entry	DMAEAc:DMAEA	Peel strength (N/cm)			
		Glass	СРІ		
1 ^a	100:0	8.64 (±0.34)	8.39 (±0.77)		
2ª	80:20	6.85 (±0.57)	7.06 (±0.11)		
3ª	60:40	4.72 (±0.06)	6.83 (±0.18)		
4 ^a	40:60	4.20 (±0.05)	6.60 (±0.21)		
5ª	20:80	3.60 (±0.07)	5.20 (±0.18)		
6 ^a	0:100	2.33 (±0.16)	3.93 (±0.46)		
7 ^b	3M Foldable OCA	5.58 (±0.21)	1.94 (±0.04)		

Table 3-22. Peel strength of the prepared OCAs with different hybrid reductant compositions (Back, *et al.*, 2022).

^aReductant content: 0.5 mol%, 4Cz-IPN content: 10 ppm, bulk polymerization: air, film curing: 10 min.

^bCommercial product of foldable OCA (CEF 3602, 3M, thickness: 50 μm).



Figure 3-33. Peel strength of the prepared OCA (black, *entry 3 in* **Table 3-22**) and commercial foldable OCA (green, *entry 7 in* **Table 3-22**) as a function of attachment time. Solid and dash lines mean peel strength on glass and CPI, respectively (Back, *et al.*, 2022).

We have optimized a photocatalyst-based visible-light-curing system and applied it to manufacture tape-type adhesives such as OCA. However, the developed visible-light-curing system can also be used for tape-type and curing-type adhesives. Therefore, we additionally fabricated curing-type adhesives by curing the pre-polymer between PET_{f} (or CPI film) rather than a release film (Figure 3-34a). Since PET_f and CPI film was transparent at visiblelight region (> 400 nm), the pre-polymer could be cured by irradiating blue light with 452 nm wavelength (Figure 3-34b). The peel strength increased with increasing HBA content (*entries 1 \sim 3 in* Figure 3-34c) because the cohesive strength of the adhesive could be enhanced by polar monomer (Table 3-12). Crosslinking also enhanced the cohesive strength of the adhesive, but excess crosslinking reduced the peel strength because of poor wettability (entries 3~8 *in* Figure 3-34c). The peel strength of CPI/PET_f was lower than PET_f/PET_f , because hydrophilic substrates have substantially better adhesive strength than hydrophobic substrates (Kowalski and Czech, 2015). It is important to note that the curing-type adhesive can be used as optically clear resin (OCR) for displays. In particular, since traditional UV-curable OCR cannot be cured under UVabsorbing material such as CPI film, visible-light-curable OCR is essential for foldable displays using CPI film as the cover window.



Figure 3-34. a) Schematic illustration for evaluating the peel strength of the curing-type adhesive. b) UV/Vis spectra of PET_f and CPI film. c) Peel strength of the prepared curing-type adhesive (Back, *et al.*, 2022). The composition of each entry was the same as the entries in Table 3-21. Peel strength was measured 10 min after curing was completed.

3.3.2. Viscoelasticity

Since OCAs for foldable displays should endure repeated folding-unfolding, their viscoelasticity should be appropriately designed. In particular, storage modulus (G') at -20 °C should be lowered for excellent folding stability under low temperatures (Campbell, *et al.*, 2017). As presented in **Table 3-23**, the prepared OCAs showed sufficiently low T_g and G' (-20 °C). Although the T_g and G' of the commercial foldable OCA were lower than our OCAs, there is potential for further improvement of our OCAs since we fabricated the OCA using minimal materials. For example, the use of acrylic monomer with low T_g (ex. nonyl acrylate) can further reduce the T_g and G' (-20 °C) of the prepared OCAs.

As the DMAEA ratio increased, the above gel content results confirmed that more crosslinking was formed, but the T_g somewhat decreased (*entries 3~8 in* **Table 3-23**). This unusual trend in T_g might result from a loose polymer network induced by DMAEA (Kaiser, 1989). When the low DMAEA ratio was employed, a polymer network was formed mainly by physical entanglement. On the other hand, as the ratio of DMAEA increased, the polymer network was formed by covalent bonding-based crosslinking instead of physical entanglement. However, the generated crosslinking-based polymer network might be looser than the entanglement-based polymer network. The low G' (25 °C, rubbery state) at the high DMAEA ratio supported the above explanation based on the loose crosslinking network.

Ent ry	Reductant	Monomer	Tg (°C)	Tan δ at 25 ℃	G' (MPa)			
	[DMAEAc]:[DMAEA]	[BA]:[HBA]			-20 °C	25 °C		
1 ^a	100:0	100:0		n/a ^b				
2 ^a	100:0	90:10	n/a ^b					
3ª	100:0	80:20	-19.7	0.315	1.423	0.099		
4 ^a	80:20	80:20	-17.8	0.270	1.934	0.080		
5 ^a	60:40	80:20	-18.7	0.262	1.441	0.082		
6 ^a	40:60	80:20	-18.8	0.218	1.132	0.070		
7 ^a	20:80	80:20	-21.0	0.209	0.587	0.060		
8 ^a	0:100	80:20	-22.1	0.200	0.388	0.059		
9°	3M Foldable OC	ĊA	-22.5	0.312	0.699	0.057		

Table 3-23. Viscoelastic properties of the prepared OCAs with different monomer/hybrid reductant compositions (Back, *et al.*, 2022).

^aBulk polymerization (air, 4Cz-IPN: 10 ppm, reductant: 0.5 mol%), film curing (10 min). ^bCured samples were too soft and did not come off cleanly from the release film. ^cCommercial product of foldable OCA (CEF 3602, 3M, thickness: 50 μm). Strain recovery and stress relaxation are the essential properties of foldable OCAs, and both should be high to achieve excellent folding stability (**Table 3-24**). As the DMAEA ratio increased, strain recovery was enhanced because of an increase in the crosslinking degree (Lee, et al., 2017). Actually, physical entanglement of the polymer network can improve strain recovery, but covalent bonding-based crosslinking is dominant for enhancing strain recovery (Lee, *et al.*, 2016). Therefore, although the prepared OCA incorporating a low DMAEA content exhibited a physical entanglement-induced polymer network, strain recovery was higher for highly crosslinked OCAs incorporating a high amount of DMAEA.

Contrary to the strain recovery trend, stress relaxation decreased as the crosslinking degree increased, and this tendency is common in OCA. In general, as strain recovery increases, stress relaxation decreases, so the crosslinking degree should be fine-tuned to achieve a high degree of both (Lee, et al., 2017). The commercial foldable OCA exhibited highly balanced strain recovery (71.1%, 25 °C) and stress relaxation (70.9%, 25 °C). Our OCAs incorporating 40 or 60% of DMAEA showed similar strain recovery (63.5 and 79.7%, 25 °C) to commercial foldable OCA, but stress relaxation was relatively low (66.2 and 54.8%, 25 °C). We believe this limitation was derived from the minimal use of materials; thus, it can be further improved in the future. As the testing temperature decreased to -20°C, strain recovery and stress relaxation decreased; we believe this limitation can also be solved by adding functional monomers/additives.

Entry .	Reductant	Monomer	Strain recovery (%)		Relaxation	ratio (%)	
	[DMAEAc]:[DMAEA]	[BA]:[HBA]	-20 °C	25 °C	-20 °C	25 ℃	
1 ^a	100:0	100:0	n/a ^b				
2ª	100:0	90:10		n/	′a ^b		
3ª	100:0	80:20	44.6	26.5	55.9	89.6	
4 ^a	80:20	80:20	64.1	54.1	45.6	69.5	
5 ^a	60:40	80:20	67.3	63.5	46.0	66.2	
6ª	40:60	80:20	73.4	79.7	43.3	54.8	
7 ^a	20:80	80:20	74.8	83.1	36.7	47.9	
8 ^a	0:100	80:20	75.8	83.5	40.9	45.2	
9°	3M Foldable C	OCA	53.5	71.1	68.5	70.9	

Table 3-24. Strain recovery and stress relaxation of the prepared OCAs with different monomer/hybrid reductant compositions (Back, *et al.*, 2022).

^aBulk polymerization (air, 4Cz-IPN: 10 ppm, reductant: 0.5 mol%), film curing (10 min). ^bCured samples were too soft and did not come off cleanly from the release film. ^cCommercial product of foldable OCA (CEF 3602, 3M, thickness: 50 μm).



Figure 3-35. Temperature sweep test results: before/after light exposure (irradiating light for 14 days by a typical display).

Since visible-light-active photocatalyst can be regenerated and continuously absorbs visible light, there is a concern that visible-light-curable OCA's properties may change under the condition of being irradiated with visible light for an extended period. Therefore, we evaluated the prepared OCA's reliability on light exposure (**Figure 3-35**). The result confirmed no significant change in the viscoelasticity of the prepared OCA after light exposure. However, since the testing condition may have been mild (light intensity or irradiating time), further research is required.

3.3.3. Folding Stability

Next, dynamic folding tests were conducted to confirm whether the produced OCAs were proper for foldable displays (**Figure 3-36~39**). All entries showed excellent folding stability without defects after folding cycles. In addition, the change in surface texture (ΔZ) did not change significantly when the number of foldings increased, indicating excellent folding stability. However, the absolute value of ΔZ increased when the testing temperature increased (Dynamic folding tests were conducted under three conditions (-20 °C for 30 K folds, 25 °C for 200 K folds, and 60 °C/93% for 50 K folds). These results might be caused by a reduction in the storage modulus of polymeric materials under an elevated temperature. This trend was the same in commercial foldable OCA (**Figure 3-40**); thus, it was confirmed that the prepared OCAs exhibited excellent folding stability comparable to the commercial product.


Figure 3-36. Dynamic folding test results (*entry 5 in* **Table 3-24**) (Back, *et al.*, 2022).



Figure 3-37. Dynamic folding test results (*entry 6 in* **Table 3-24**) (Back, *et al.*, 2022).



Figure 3-38. Dynamic folding test results (*entry 7 in* **Table 3-24**) (Back, *et al.*, 2022).



Figure 3-39. Dynamic folding test results (*entry 8 in* **Table 3-24**) (Back, *et al.*, 2022).



Figure 3-40. Dynamic folding test results (*entry 9 in* **Table 3-24**) (Back, *et al.*, 2022).

3.4. Preparation and Characterization of UV-blocking OCAs

3.4.1. UV-Protection

Finally, we manufactured UV-blocking OCAs by adding UV absorber into the pre-polymer obtained from the bulk polymerization. There were a lot of UV absorbers (formamidine, benzophenone, benzotriazole, triazine, and oxanilide) (Pospišil, et al., 2000), and we used cvanoacrylate-type UV absorber (UV absorber 2 in Figure 3-41). Although UV absorber 2 exhibited excellent solubility to acrylic monomer and absorbed light with wavelengths under 350 nm, it could not cover the wavelengths from 350 to 400 nm. Therefore, we employed an additional UV absorber to cover the full spectrum of UV rays (UV absorber 1 in Figure 3-41). The contents of UV absorbers 1 and 2 were optimized to minimize the use of additives (Figure 3-42). When the 0.3 phr of UV absorber 1 and 1 phr of UV absorber 2 were employed simultaneously, the UV-blocking OCA could be successfully manufactured. The prepared UVblocking OCA showed excellent transparency ($T_{455 \text{ nm}} \sim 100\%$) and UV protection ($T_{365 \text{ nm}} = 1.6\%$), and such superior transparency and UV protection have seldom been achieved simultaneously in acrylate-based composites (Liu, et al., 2012, Loste, et al., 2019, Zhang, et al., 2012).



Figure 3-41. UV/Vis spectra of the UV absorbers we used (Back, et al., 2022).



Figure 3-42. UV/Vis spectra of the cured UV-blocking OCAs incorporating a) one UV absorber and b) two UV absorbers (Back, *et al.*, 2022). The monomer, reductant, and photocatalyst content were the same with *entry 5 in* **Table 3-24**. The film curing time was set as 30 min.



Figure 3-43. Conversion of the film curing using different light sources (Back, *et al.*, 2022). The monomer, reductant, and photocatalyst content were the same with *entry 5 in* **Table 3-24**. For UV curing, 1000 ppm of PI (Irgacrue 184) was used instead of photocatalyst, and UV-induced bulk polymerization was conducted under argon conditions. 0.3 phr of UV absorber 1 and 1 phr of UV absorber 2 were added after bulk polymerization.

UV-blocking OCA was prepared by film curing of pre-polymer containing UV absorbers, and the curing rate was compared using two different light sources; 365 nm (UV) and 455 nm (blue light). As presented in **Figure 3-43**, OCA without UV absorbers was cured within 5 minutes for both light sources. However, adding UV absorbers for both cases decreased the film curing rate. Furthermore, the film curing rate decreased significantly with UV-curing than with blue light-curing because UV absorbers blocked most UV rays. Therefore, although the curing time increased from 10 min to 30 min, blue light was much more efficient for curing UV-blocking OCAs than UV.

3.4.2. Physical Properties and Adhesive Performances

We next evaluated the physical properties and adhesive performances of the prepared UV-blocking OCAs (**Table 3-25**). For preparing UV-blocking OCAs, we employed the optimal composition of hybrid reductant (40 or 60% of DMAEA) exhibiting comparable peel strength and strain recovery to commercial foldable OCA. After adding UV absorbers, the gel content did not change significantly, but the peel strength slightly decreased. Compared to the commercial foldable OCA (5.58 N/cm, **Table 3-22**), the prepared UV-blocking OCAs exhibited low peel strength to the glass. However, peel strength to CPI was more than twice as high in the prepared UV-blocking OCAs as in commercial foldable OCA (1.94 N/cm, **Table 3-22**).

Table 3-25. Physical properties and adhesive performances of the prepared UVblocking OCAs (Back, *et al.*, 2022). 0.3 phr of UV absorber 1 and 1 phr of UV absorber 2 were added after bulk polymerization. The film curing time was set as 30 min.

Entry	DMAEAc:DMAEA	Gel content (%)	Peel strength (N/cm)			
			Glass	CPI		
1	60:40	72.7 (±1.0)	2.75 (±0.27)	5.42 (±0.50)		
2	40:60	72.9 (±1.3)	2.41 (±0.28)	5.37 (±0.26)		

3.4.3. Viscoelasticity

As a result of evaluating the viscoelasticity of UV-blocking OCAs (**Table 3-26**), the storage modulus at -20°C decreased when UV absorbers were added (w/o UV absorbers: 1.441 MPa and 1.132 MPa, **Table 3-23**). These results are because T_g was lowered by adding UV absorbers to OCA (w/o UV absorbers: - 18.7 °C and -18.8 °C, **Table 3-23**), but the cause of T_g reduction is still unclear.

Table 3-26. Viscoelastic properties of the prepared UV-blocking OCAs (Back, *et al.*, 2022). Detailed conditions for preparing UV-blocking OCAs were the same with **Table 3-25**.

Ent _ ry	Reductant	Monomer	Tg (°C)	Tan ð at 25 ℃	G' (MPa)	
	[DMAEAc]:[DMAEA]	[BA]:[HBA]			-20 °C	25 °C
1	60:40	80:20	-23.5	0.227	0.420	0.066
2	40:60	80:20	-25.8	0.225	0.419	0.072

We next assessed strain recovery and stress relaxation of the UV-blocking OCAs (**Table 3-27**). When UV absorbers were added to OCA, strain recovery slightly increased (w/o UV absorbers: 63.5% and 79.7% at 25 °C, **Table 3-24**), while stress relaxation somewhat decreased (w/o UV absorbers: 66.2% and 54.8% at 25 °C, **Table 3-24**). These results indicated that adding UV absorbers to the OCA increased its stiffness.

Table 3-27. Strain recovery and stress relaxation of the prepared UV-blocking OCAs (Back, *et al.*, 2022). Detailed conditions for preparing UV-blocking OCAs were the same with **Table 3-25**.

Ent ry	Reductant	Monomer	Strain recovery (%)		Relaxation ratio (%)	
	[DMAEAc]:[DMAEA]	[BA]:[HBA]	-20 °C	25 °C	-20 °C	25 °C
1	60:40	80:20	71.4	79.7	49.9	54.9
2	40:60	80:20	73.4	81.1	44.9	51.2

3.4.4. Folding Stability

We finally assess the folding stability of the prepared UV-blocking OCAs via the dynamic folding test (**Figure 3-44 and 45**). It is important to note that, independent of test conditions, UV-blocking OCA with 60% of DMAEA showed excellent folding stability with no defects and small changes in ΔZ . These results indicated that the prepared UV-blocking OCA nearly satisfied the requirements of foldable displays. In addition, although a defect was observed in one specimen, the UV-blocking OCA with 40% of DMAEA also exhibited sufficient folding stability to be used for foldable displays. However, since the dynamic folding tests were conducted using simulated specimens, further research using actual foldable displays should be required.



Figure 3-44. Dynamic folding test results (*entry 1 in* **Table 3-27**) (Back, *et al.*, 2022).



Figure 3-45. Dynamic folding test results (*entry 2 in* **Table 3-27**) (Back, *et al.*, 2022).

3.5. Conclusions

In the last section, we designed the visible-light-curable UV-blocking OCAs for foldable displays. Firstly, we optimized the visible-light-active photocatalyst-based polymerization using various photocatalysts and reductants with different HOMO levels. We found that the optimal composition (photocatalyst: 10 ppm of 4Cz-IPN, reductant: 0.5 mol% of DMAEAc) showed excellent polymerization behavior under both argon/air conditions. After that, we employed the hybrid reductant to adjust the OCA's crosslinking degree with minimized additive-type reductant (DMAEAc). By adjusting the ratio of DMAEAc and DMAEA, the gel content, peel strength, strain recovery, and stress relaxation could be controlled, and an optimal composition was derived (40 or 60% of DMAEA). At last, the UV-blocking OCAs were prepared by adding UV absorbers into the optimal composition, showing excellent transparency and UV protection. It was confirmed that visible light-curing was much more efficient for curing UV-blocking OCAs than traditional UV-curing. Furthermore, the adhesive strength and viscoelasticity of the produced UVblocking OCAs were suitable for foldable displays. Remarkably, the UVblocking OCA incorporating 60% of DMAEA showed excellent folding stability regardless of test conditions, indicating that the potential for application to foldable displays was very high.



Conclusions

1. Conclusions

Here, we developed photocatalyst-based visible light-curable acrylic PSA for display applications. Although visible-light-active photocatalyst can initiate polymerization in a smaller amount than traditional UV-active PI due to its regeneration characteristics, the content of photocatalyst should be further lowered for manufacturing OCAs for displays. Therefore, we developed three strategies to facilitate visible-light-active photocatalyst's catalytic cycle; driving the catalytic cycle by 1) typical monomers used for acrylic PSAs or 2) additives. 3) Optimizing the catalytic cycle using various photocatalysts and additives. After that, various acrylic PSAs were adequately designed for display applications, considering many factors (T_g , crosslinking degree, adhesive strength, viscoelasticity, and minimizing additives).

1.1. Driving the Catalytic Cycle by Typical Monomer for General PSA

For the first strategy, we successfully manufactured visible-light-curable acrylic PSAs employing photocatalyst and typical monomer. N-vinyl-based monomer, a functional monomer that enhances the cohesive strength of acrylic PSAs, was employed to drive the reductive quenching cycle. For an efficient catalytic cycle, 4DP-IPN was used as photocatalyst because of its 1) excellent triplet 2) visible generation, strong light absorption, 3) high photo/electrochemical stability, and 4) proper redox potentials. Visible lightcurable acrylic PSA was manufactured by bulk polymerization and film curing processes, and N-vinyl-based monomer vastly improved the polymerization rate. A plausible mechanism for initiation by N-vinyl-based monomer was also proposed. After that, we evaluated the viscoelasticity, physical properties, and adhesive performances of the prepared acrylic PSAs with different monomer compositions. It was confirmed that the properties of the visible-light-curable acrylic PSAs were adjusted in a wide range. Remarkably, although the prepared visible-light-curable acrylic PSA showed poor transparency due to the high amount of photocatalyst (50 ppm), their adhesive strength was successfully controlled from 0.40 N/cm to 9.90 N/cm. In other words, the prepared visible-light-curable acrylic PSAs could be utilized for displays as release film or back film/plate rather than OCA.

1.2. Driving the Catalytic Cycle by Additives for OCA

For the second strategy, the catalytic cycle of 4DP-IPN was facilitated by additives to produce the OCA for mobile displays. The addition of an α improved photopolymerization behavior, haloester vastly and the disadvantages (the slow polymerization rate and poor transparency) of the photocatalyst-based PSA were addressed. Three types of α -haloester (DBM, EBP, and EBiB) were tested, and DBM was chosen as the best to drive the oxidative quenching cycle with 4DP-IPN because of their redox potentials. We optimized the content of 4DP-IPN (10 ppm) and DBM (0.1 mol%), exhibiting excellent curing rate and transparency. The resulting PSA showed excellent adhesive properties (peel strength: 2.8 N/cm, loop tack: 5.2 N/cm, holding time > 100 h) and optical transparency (approximately 100% at 400 nm), and these properties were comparable to those of conventional OCA for mobile displays.

1.3. Optimization of the Catalytic Cycle with Various Photocatalysts and Additives for UV-blocking OCA

For the last strategy, we fabricated the most effective visible light-curing system exhibiting a fast polymerization rate and strong oxygen tolerance to manufacture UV-blocking OCA. Various photocatalysts and reductants with different HOMO levels were employed, and the optimal combination was found (photocatalyst: 4Cz-IPN, reductant: DMAEAc). After that, we employed the hybrid reductant to control the crosslinking degree of OCA and reduce the use of additive-type reductant (DMAEAc). The gel content, peel strength, strain recovery, and stress relaxation could be controlled by the ratio of the hybrid reductant; thus, the optimal ratio was obtained (DMAEA: 40% or 60%). Finally, we prepared the UV-blocking OCAs by adding UV absorbers to the optimal OCA composition. It was also verified that visible light-curing was far more efficient for curing UV-blocking OCAs than typical UV-curing. The prepared UV-blocking OCAs showed excellent transparency, UV protection, peel strength, and viscoelasticity for foldable displays. Notably, when 60% of DMAEA was employed, the UV-blocking OCA exhibited exceptional folding stability under all test conditions (25 °C, -20 °C, and 60 °C/93%), closely meeting the requirements for foldable displays. Conclusively, these results indicated that the developed visible light-curing system was practically efficient for fabricating the UV-blocking OCA with high potential for application to actual foldable displays.



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List of Publications

This Ph.D. dissertation is based on the following publications.

I. <u>Back, J. H.</u>, Kwon, Y. H., Roldao, J. C., Yu, Y. C., Kim, H. J., Gierschner, J., Lee, W. J., and Kwon, M. S., 2020, Synthesis of Solvent-Free Acrylic Pressure-Sensitive Adhesives via Visible-Light-driven Photocatalytic Radical Polymerization without Additives, *Green Chemistry*, 22 (23): 8289-8297

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III. <u>Back, J. H.</u>, Kwon, Y. H., Cho, H. J., Lee, H. S., Ahn, D. W., Kim, H. J., Yu, Y. C., Kim, Y. D., Lee, W. J., Kwon, M. S., 2022, Visible-Light-Curable Acrylic Resins toward UV-Light-Blocking Adhesives for Foldable Displays, *Advanced Materials*, Accepted paper (https://doi.org/10.1002/adma.202204776) 초 록

점착제는 가벼운 압력으로 다양한 기판에 접착하는데 사용되는 고분자 재료이고, 화학 조성에 따라 고무계, 아크릴계, 실리콘계 점착제로 분류된다. 아크릴계 점착제는 우수한 물성 (내산화성, 투명성, 황변저항성, 접착강도 등)을 바탕으로 모바일 디스플레이 조립에 필수적인 소재가 되었으며, 디스플레이 적용 부위마다 다른 물성이 요구된다. 예를 들어, 발광층 위쪽에 위치하는 점착제는 일반적으로 우수한 투명도가 요구된다 (투명 점착필름). 반면에 이형 필름용 점착제와 후면 필름/플레이트용 점착제는 각각 낮은 점착력과 높은 점착력이 요구된다.

아크릴계 점착제의 가장 중요한 장점 중 하나는 광중합이 가능하다는 것인데, 주로 자외선 활성 광개시제를 통해 제조되었다. 하지만 가시광선 경화는 자외선 경화와는 다르게 자외선이 차단된 환경에서도 경화가 가능하다는 큰 장점이 있다. 따라서 본 연구에서는 모바일 디스플레이용 광경화형 아크릴 점착제를 새롭게 개발하였으며, 가시광선 조건에서 중합을 개시하기 위해 가시광 활성 광촉매를 사용했다. 중합에 필요한 광촉매 양은 광개시제보다 훨씬 적지만, 모바일 디스플레이용 투명 점착필름을 제조하기
위해서는 가시광 활성 광촉매 사이클의 구동을 촉진시켜 광촉매 함량을 더 줄여야 한다. 본 연구에서는 광촉매의 효율을 향상시키기 위해 세 가지 전략을 사용했고 그 후에는 여러 요인 (유리전이온도, 점탄성, 가교도, 접착강도, 첨가물양 등)을 고려하여 모바일 디스플레이용 아크릴 점착제를 체계적으로 설계했다.

첫 번째, 아크릴 점착제에 일반적으로 사용되는 단량체를 광촉매 촉매 사이클 구동에 사용해보았다. 질소-비닐계 단량체는 아크릴계 점착제의 응집력을 향상시킬 때 사용되는 단량체이고, 환원제로도 작용할 수 있어서 촉매의 환원성 소광 사이클을 촉진할 수 있었다. 가시광선 경화형 점착제는 두 단계 (벌크 중합 및 필름 경화)로 제조되었고 광촉매로는 4DP-IPN을 사용했다. 실험 결과, 질소-비닐계 단량체 (1-Vinyl-2-pyrrolidinone) 투입은 개시를 촉진시켜 중합 속도를 크게 향상시켰다. 이 과정에서 다른 단량체 조성을 달리하여 다양한 점착제를 제조할 수 있고, 이들의 특성 (점탄성, 물리적 물성 및 접착 성능)을 광범위하게 조절할 수 있었다. 제조된 가시광선 경화형 점착제는 많은 촉매 양 (50 ppm)이 요구되어 투명 점착필름으로는 사용 불가능했지만, 낮은 점착력을 요구하는 이형 필름이나 높은 점착력을 요구하는 후면 필름/플레이트 등에는 활용 가능할 것으로 기대되었다.

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두 번째, 촉매 사이클 구동을 더욱 활성화시키고자 할로에스터 계열의 첨가제를 사용했다. 할로에스터는 4DP-IPN의 산화성 소광 사이클을 촉진하는 것으로 알려진 산화제이고, 본 실험에서는 3 가지의 할로에스터를 평가해보았다. 실험을 통해 도출된 최적의 조성 (4DP-IPN: 10 ppm, 디에틸 2-브로모-2-메틸말로네이트; DBM: 0.1 mol%)을 가시광선 경화형 투명 점착필름 제조에 사용했을 때, 제조된 점착제는 우수한 접착 성능과 빠른 중합 속도를 나타냈다. 특히 제조된 점착제는 낮은 4DP-IPN 함량 (10 ppm) 에서도 우수한 중합 거동을 나타내 이전 연구대비 투명도를 대폭 개선할 수 있었다. 따라서 해당 시스템은 모바일 디스플레이용 투명 점착필름에 활용 가능할 것으로 기대되었다.

세 번째, 광촉매 사이클을 최적화하고 이를 통해 가시광선 경화형 자외선 차단 투명 점착필름을 제조해보았다. 에너지 준위가 다른 다양한 광촉매와 환원제들을 평가했으며, 이들의 최적 조합을 도출했다 (4Cz-IPN: 10 ppm, 2-(디메틸아미노)에틸 아세테이트; DMAEAc: 0.5 mol%). 다음으로는 DMAEAc와 구조적으로는 유사하지만 가교결합을 유도하는 또 다른 환원제 (2-(디메틸아미노)에틸 아크릴레이트; DMAEA)를 추가적으로 사용했다. 폴더블 디스플레이용 투명 점착필름의 가교도 조절을 위해 이 두

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가지 환원제 (DMAEAc 및 DMAEA)를 동시에 사용하는 하이브리드 환원제 시스템을 도입했으며, 그 조성을 최적화하였다. 그리고 도출된 최적 조성에 마지막으로 자외선 흡수제를 첨가함으로써 자외선 차단 투명 점착필름을 제조했다. 제조된 자외선 차단 투명 점착필름은 우수한 성능 (투명성, 자외선 차단, 박리강도 및 점탄성)을 보였고, 다양한 환경 (25 ℃, -20 ℃, 60 ℃/93%)에서도 높은 폴딩 안정성을 나타냈다. 따라서 본 연구를 통해 제조된 자외선 차단 투명 점착필름은 실제 폴더블 디스플레이에도 충분히 적용 가능할 것으로 기대되었다.

키워드 : 광촉매, 가시광경화, 아크릴 점착제, 투명 점착필름, 자외선 차단 투명 점착필름, 모바일 디스플레이

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