

Visible-Light-Curable Acrylic Resins toward UV-Light-Blocking Adhesives for Foldable Displays

Jong-Ho Back, Yonghwan Kwon, Hyeju Cho, Huesoo Lee, Dowon Ahn, Hyun-Joong Kim, Youngchang Yu,* Youngdo Kim,* Wonjoo Lee,* and Min Sang Kwon*

Current technological advances in the organic light-emitting diode panel design of foldable smartphones demand advanced adhesives with UV-blocking abilities, beyond their conventional roles of bonding objects and relieving deformation stress. However, optically clear adhesives (OCAs) with UV-blocking ability cannot be prepared using conventional UV-curing methods relying on a photoinitiator. Herein, a new acrylic resin that can be efficiently cured using visible light without oxygen removal is presented, which may be used to develop UV-blocking OCAs for use in current flexible displays. A novel photocatalyst and a specific combination of additives facilitate sufficiently rapid curing under visible light in the presence of UV-absorbers. Only a very small amount of the highly active photocatalyst is required to prepare UV-blocking OCA films with very high transparency in the visible region. Using this system, a UVblocking OCA that nearly meets the specifications of an OCA used in commercialized foldable smartphones is realized. This technology can also be utilized in other applications that require highly efficient visible light curing, such as optically clear resins, dental resins, and 3D/4Dprintable materials.

J.-H. Back, H. Cho, H. Lee, D. Ahn, Y. Yu, W. Lee Center for Advanced Specialty Chemicals Korea Research Institute of Chemical Technology (KRICT) Ulsan 44412, Republic of Korea E-mail: ycyu@krict.re.kr; winston@krict.re.kr J.-H. Back, H.-J. Kim Department of Agriculture Forestry and Bioresources Seoul National University Seoul 08826, Republic of Korea Y. Kwon, M. S. Kwon Department of Materials Science and Engineering Seoul National University Seoul 08826, Republic of Korea E-mail: minsang@snu.ac.kr Y. Kwon Department of Materials Science and Engineering Ulsan National Institute of Science and Technology (UNIST) Ulsan 44919, Republic of Korea Y. Kim Samsung Display Co., Ltd. Cheonan 31086, Republic of Korea E-mail: colour.kim@samsung.com

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1. Introduction

The field of flexible electronics has emerged as a key future technology that enables a variety of novel applications, such as flexible lighting and displays,^[1-3] wearable sensors for health monitoring,^[4–6] implantable electronics for medical diagnosis and treatment,^[7,8] soft robotics,^[9-11] and conformable energyharvesting devices.^[12-14] An adhesive is one of the most essential components of a flexible electronic device. Beyond the conventional role of bonding two objects,^[15,16] it can also prevent the destruction of the device by relieving the "tensile and compressive stresses" generated when the device is deformed.^[17,18] Moreover, the adhesive is further required to have additional functional properties depending on the final device; for example, it is expected to have optical transparency,^[19] electrical/thermal conductivity.^[20,21] biocompatibility,^[22-24] biodegradability,^[25–27] and other properties.

The importance of adhesives in flexible devices can be clearly seen in the recently developed foldable smartphones. In 2019, the world's first foldable smartphone was launched, pioneering the development of a flexible smartphone that breaks away from the classic bar-type smartphone.^[28] A smartphone is composed of many thin layers with a complex architecture, and the adhesive plays an important role (Figure 1a). Particularly, in a foldable phone, the adhesive is required to aid the dissipation of the generated stress to prevent delamination and/or warping of the films even at large external deformations.^[29,30] Moreover, the adhesive should have sufficient adhesion, flexibility, and elasticity in extreme environments (high/low temperature and/ or high humidity), as well as be optically transparent.^[19] Hence, a new type of adhesive with the aforementioned advanced properties, which are not normally required in a conventional rigid phone, was specially developed for the foldable phone (previously reported optically clear adhesives (OCAs) for flexible devices are summarized in Table S1, Supporting Information). For the current foldable display, a novel technology was developed that reduces the power consumption of the panel by 25%. Owing to the unique panel design of the current foldable display, the use of an additional polarizer layer, which is normally used to prevent the panel from reflecting external light, can be eliminated (Figure 1a).^[31] However, interestingly, www.advancedsciencenews.com

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Figure 1. a) Device structure of a foldable smartphone with conventional organic light-emitting diode (OLED) panel (left) and advanced OLED panel (right). b) Proposed mechanism for photocatalyzed visible-light-driven free radical polymerization in the presence of sacrificial reductants. Here, PC, ISC, ET, and PET denote photocatalyst, intersystem crossing, electron transfer, and photo-induced electron transfer, respectively. c) Molecular structures and experimentally evaluated redox potentials of photocatalysts (PCs) and sacrificial reductants. Calculated HOMO and LUMO energies of each PCs and reductants are also shown. The ground redox potentials (E_{red}^0 and E_{ox}^0) were measured against standard calomel electrode (SCE) in CH₃CN using cyclic voltammetry (CV). The excited reduction potential (E_{red}^*) was obtained by $E_{red} = E_{00} - E_{red}^0$; $E_{00}(S_1)$ and $E_{00}(T_1)$ were evaluated from the onset of photoluminescence (PL) and gated PL spectra of PCs in ethyl acetate at 65 K, respectively. [†]The redox potentials of the ground state were evaluated from the half-peak potentials ($E_{p/2}^0$) due to their irreversible CV cycle.

this technological advance demands an adhesive with UV-blocking ability to serve the role of the polarizer that protects the panel by absorbing UV from the outside.^[32]

Conventional adhesives used in smartphones are OCAs that are prepared by the UV-light curing of acrylic resins:^[33] for a successful transmission of the light emerging from the panel to the outside, adhesive films should not absorb visible light. As UV-blocking OCAs contain additives with strong UV-light absorption properties, which prevent effective UV-light absorption by the photoinitiator, they cannot be prepared by the conventional photocuring method. Although thermal curing could be utilized as an alternative process,^[34,35] this method suffers significantly from inherent drawbacks, such as the inhomogeneity of the cured film, emission of volatile organic compounds, difficulty in producing large-area films, and thermal damages. We therefore envisioned that the development of a new acrylic resin that can be effectively cured through visible-light irradiation would be an excellent solution to this issue. Furthermore, the new system would be more beneficial for addressing the inherent issues of the current UV-curing systems, such as their oxygen sensitivity.^[36]

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level loading of the PC is required. We thus developed a PC that effectively generates long-lived triplet excited states (T_1) (Figure 1b). In fact, the population of T_1 plays a crucial role in photoredox catalysis, as T_1 shows a lifetime long enough to enable efficient PET.^[60,61] Furthermore, the T_1 is known to be less susceptible to back electron transfer (BET), which reduces the efficiency of the catalyst.^[60]

To minimize additives and ensure oxygen-tolerance, a reductive quenching cycle was selected as the mechanistic pathway for the visible-light curing of the system (Figure 1b). Note that established reaction processes in photoredox catalysis include a reductive and an oxidative quenching cycle.^[59] Tertiary amines can be the most suitable sacrificial reductants here as they can have additional roles such as initiator and oxygen scavenger. In the reductive cycle, PET first occurs between the PC and the amine-based sacrificial reductant to afford a PC radical anion (PC*) and amine radical cation (R₃N*+). Subsequently, R₃N*+ loses a proton (H⁺) to generate an α -amino radical species that acts as an initiator of the free radical polymerization of the monomer.^[36] Tertiary amines also reduce oxygen-inhibition. They can react with unreactive peroxyl radicals produced by the reaction of growing radical species and oxygen, converting them to reactive α -amino radical species.^[62,63] Further, an electron transfer reaction between PC⁻ and O₂ regenerates the ground-state PC,^[64,65] allowing the catalytic cycle to proceed smoothly.

Considering these facts, four PCs with a strongly twisted donor-acceptor (D-A) structure were prepared (Figure 1c). Molecules with such a structure usually generate long-lived T₁ in an effective manner because they can satisfy both the requirements of a small energy gap and the orthogonality rule.^[66] In fact, according to previous studies by our group^[66–69] and others,[70-75] 4Cz-IPN and 4DP-IPN were considered as representative PCs that have such a structure because of their significantly high photocatalytic performance in a variety of chemical reactions involving a reductive or oxidative cycle. In addition to these two PCs, we designed two additional PCs with a significantly lower highest occupied molecular orbital (HOMO) energy to facilitate PET between the PC and amine-based sacrificial reductant and thus enhance the catalytic performance; since the PET between PC and the sacrificial reducing agent is usually located in the Marcus "normal region", reducing the HOMO energy of PC increases the driving force $(-\Delta G_{PET})$ and thus the electron transfer rate.^[76] As the HOMO is localized in the donor moiety in the strongly twisted D-A type molecule, we introduced a strong electronwithdrawing group (i.e., -CN group) into the donor group to reduce the HOMO energy (Figure 1c). A full description of the synthesis and characterization of the PCs (i.e., ¹H NMR spectra, UV-vis absorption spectra, photoluminescence (PL) emission spectra, and cyclic voltammograms) are provided in the Supporting Information. According to our expectations, the introduction of the electron-withdrawing -CN groups indeed increased the excited state reduction potentials of the PCs (E_{red}^{*} (PC)), consistent with the trend of the HOMO energies of the PCs predicted by density functional theory (DFT) calculations (Figure 1c). Further, four tertiary amines with different oxidation potentials were selected as sacrificial reductants (Figure 1c).

and realized UV-blocking OCAs that can be applied in flexible displays for the first time. Most importantly, a novel photocatalyst (PC) and a combination of additives, which facilitates sufficiently rapid curing under visible light in the presence of UV-absorbers, are presented. Owing to the high catalytic activity of the PC, only an extremely small amount of it (10 ppm with respect to monomers) was used to prepare UV-blocking OCA films. This allowed the films to exhibit very high optical transparency in the visible-light region. Screening of various aminebased reductants revealed that the role of amine additives is not limited to being sacrificial reductants, as they can serve as initiators, oxygen scavenger, and cross-linkers. The understanding of the role of amines helped us to optimize the structure of amine-based reductants, and thus minimize the use of additives (i.e., an external cross-linker and/or initiator) and also enhance the curing rate. Furthermore, we observed strong

also enhance the curing rate. Furthermore, we observed strong oxygen-tolerance behavior with a specific combination of the PC and sacrificial reductants, which has been rarely observed, only in systems employing special agents, such as boron derivatives,^[37,38] thiol derivatives,^[39,40] and chain-transfer agent.^[41–43] A mechanism for the oxygen-tolerance behavior is also proposed through experimental studies combined with quantum chemical calculations. Using this system, we successfully developed a UV-blocking OCA that nearly meets the specifications of an OCA used in a commercialized foldable smartphone. We believe that this technology would not be limited to the development of UV-blocking OCAs, but could be widely extended to a variety of applications that require a highly efficient visible-light-curing process, such as in the development of optically clear resins,^[44] dental resins,^[45] and 3D/4D-printable materials.^[46]

In this study, we developed a new acrylic resin that can be

efficiently cured using visible light without oxygen removal

2. Results and Discussion

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2.1. Design Strategy

Since the pioneering studies on photoredox catalysis by MacMillan,^[47] Stephenson,^[48] and Yoon^[49] in 2008, visible light has been actively used as an energy source for a variety of organic reactions. This strategy was subsequently combined with prevalent polymerization reactions, resulting in considerable advancement in visible-light-driven polymerization processes relying on the photoinduced electron transfer (PET) between PC and substrate.^[50-57] Despite the recent intensive efforts, it is still very difficult to achieve a visible-light-curing resin system for producing UV-blocking OCAs because of the following reasons: i) a high loading of the colored PC, which lowers the optical transparency of the resultant OCA;^[55] ii) the use of additives that are colored and/or contain sulfur or halogen atoms,[58,59] which are not permitted for use in electronic devices; iii) a slower curing rate compared to that of a UV-light/photoinitiator system; and iv) ambiguous oxygen-tolerance. In fact, the oxygen-tolerance of a photoredox-mediated polymerization is known to be very sensitive to reaction conditions.^[36]

To ensure optical clarity in the visible region as well as a sufficiently high curing rate, a visible-light-curing system that has a sufficiently fast polymerization rate even at ppm



2.2. Bulk Polymerization

Using the four PCs and sacrificial reductants, we studied the visible-light-driven bulk polymerization of acrylic monomers, which is the first step in the preparation of OCAs. Note that acrylic OCAs are usually prepared by the photo-mediated bulk polymerization of acrylic monomers followed by a subsequent photoinduced film curing process (Figure S1, Supporting Information).^[33] In this study, *n*-butyl acrylate (BA) and 4-hydroxybutyl acrylate (HBA) were chosen as monomers, because they are known to yield OCAs suitable for a foldable display.^[33] The BA is a monomer with a low glass transition temperature (T_{g}) that imparts considerable flexibility to OCAs even at low temperatures, while HBA is used to impart good cohesive strength to OCAs (Table S2, Supporting Information). As a control experiment, we first conducted the bulk polymerization of a mixture of BA and HBA using a conventional photoinitiator (i.e., 1000 ppm of Irgacure 184; Table S5, Supporting Information, for details) under argon atmosphere and UV-light illumination (365 nm, 8 W, 20 s; entry 6, Table S5, Supporting Information). Continuous light irradiation provided poly(BA-co-HBA) with a moderate conversion (5.22%) and high molecular weight ($M_n = 1319 \text{ kg mol}^{-1}$). No polymerization occurred when the same reaction was performed without degassing, which clearly confirmed that conventional photoinitiator-mediated photocuring of the BA/HBA mixture is not resistant to oxygen, as expected (entry 5, Table S5, Supporting Information).

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2.3. Optimization of PC and Reductant

To evaluate the catalytic performances of the prepared PCs, we conducted the same polymerization using 10 ppm of each PC in the presence of DMAEAc (5000 ppm) chosen as the sacrificial reductant under argon atmosphere and 455 nm light-emitting diode (LED) irradiation (18 W, 30 s; Table 1). Significantly different results were obtained for different PCs, among which, 4Cz-IPN showed the highest catalytic performance, which is somewhat unexpected (vide infra). In fact, PCs with lower HOMO energies were expected to perform better. As shown in Table 1, under the polymerization conditions without degassing, no polymerization was observed with most of the PCs except in the cases of 4Cz-IPN and 4-p,p-DCDP-IPN. Although 4-p,p-DCDP-IPN exhibited powerful oxygen-acceleration behavior, and the monomer conversion was considerably increased from 6.1 to 24.0% in the presence of oxygen, it had solubility issues in the monomer mixture (Figure S5, Supporting Information). The 4Cz-IPN exhibited the best performance among the PCs without any solubility issue. It provided a significantly high conversion (23.0%) even under nondegassed conditions, with the conversion being slightly higher than that obtained under argon atmosphere. For comparison, the same bulk polymerizations were also performed in an oxidative quenching cycle where alkyl bromide was employed as an initiator instead of DMAEAc (Table S5, Supporting Information). No polymerization occurred in non-degassed conditions, indicating that reductive quenching cycle is a better choice for this case, as expected (see Section 2.1., "Design strategy").

Pre-polymer

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Table 1. Results of the bulk polymerizations with various PCs and redu	uctants.
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	от страници и страници От страници и	H + O PC (10 pp) Reductant BA 455 nm LE 30 s, r.t. u	$\begin{array}{c} m \\ \hline (5000 \ ppm) \\ \hline Ds \ (18 \ W) \\ nder \ argon \ or \ air \\ \end{array} + PC + unreacted \ monormality \\ \end{array}$	OH OH	
Entry	PC [10 ppm] Reductant [5000 ppm]		Conversion [%]		
		=	Under argon	Under air	
1	-	-	No separable polymer	No separable polymer	
2	-	DMAEAc	No separable polymer	No separable polymer	
3	4DP-IPN	DMAEAc	6.7	No separable polymer	
4	4Cz-IPN	DMAEAc	20.0	23.0	
5	4-o,p-DCDP-IPN	DMAEAc	1.3	No separable polymer	
6	4-p,p-DCDP-IPN	DMAEAc	6.1	24.0	
7	4Cz-IPN	-	3.8	No separable polymer	
8	4Cz-IPN	DIPEA	4.0	No separable polymer	
9	4Cz-IPN	TEA	18.8	14.8	
10	4Cz-IPN	DMBA	11.2	15.7	

Composition of monomer mixture was fixed as follows: [BA]:[HBA]:[Reductants]:[PC] = 80:20:0.5:0.001. The bulk polymerizations were conducted under blue LED illuminations (455 nm, 18 W, 30 s; see Supporting Information for details) and argon or air atmosphere. Conversions were gravimetrically evaluated. Full details of the bulk polymerizations are given in Tables S7 and S8, Supporting Information.





Figure 2. a) UV-vis absorption and steady-state PL of PCs $(1.0 \times 10^{-5} \text{ M})$ in ethyl acetate at room temperature. The inset shows the PL decay of PCs $(1.0 \times 10^{-5} \text{ M})$ in an ethyl acetate. Fluorescence lifetimes of prompt and delayed component are also shown. PL spectra were obtained from non-degassed (dotted line) or degassed (solid line) solution of the PCs by purging with argon for 10 min. The PL quantum yield (Φ_{PLQY}) of PCs were determined through a relative method using Φ_{PLQY} of coumarin 153 $(1.0 \times 10^{-5} \text{ M})$ in ethanol solution as a reference.^[92] b) Stern-Volmer plots for the PL quenching of a series of PCs in ethyl acetate by DMAEAc (left) and for the PL quenching of 4Cz-IPN in ethyl acetate by various tertiary amine reductants (right). c) Results of kinetics simulation for the variations of the relative populated of the lowest singlet excited state (S₁; left) and triplet excited PCs ($6.9 \times 10^{-5} \text{ M}$) over time after turn-on continuous 455 nm irradiation (see Supporting Information for more detail).

We then investigated the effects of the sacrificial reductants on the catalyst performance (Table 1 and Table S6, Supporting Information). For this, 4Cz-IPN was used as the PC at 10 ppm. Among the four reductants (i.e., DIPEA, TEA, DMBA, and DMAEAc), DMAEAc provided the highest conversion in both ambient and inert conditions. The results were completely different from our expectations because DMAEAc has the lowest HOMO energy among the amines, and electron transfer from it to PC was expected to be the slowest. The DIPEA with the highest HOMO energy exhibited the poorest performance, and no polymers were obtained when the reaction was conducted without degassing.

2.4. Origin of the Catalytic Performance

Before investigating the curing of the OCA film, mechanistic studies were performed to understand the origin of the unexpected results obtained in the bulk polymerization reactions using different PCs and amines: i) 4Cz-IPN exhibited better catalytic performance than the other PCs with lower HOMO energies, ii) DMAEAc with the lowest HOMO energy was the best sacrificial reductant among the amines, and iii) strong oxygen-tolerance behavior was observed for 4Cz-IPN in the presence of DMAEAc.

When the sacrificial reductant is the same, the catalyst performance is solely determined by the PET and BET between the PC and sacrificial reductant. Contrastingly, the rate of PET is described by Equation (1):

$$\nu_{\text{PET}} = k_{\text{PET}} [\text{PC}^*][\text{S}] \tag{1}$$

where [PC^{*}] is the concentration of the PC in the excited state and [S] is the concentration of the sacrificial reductant. First, to determine the rate constant of the PET (k_{PET}) in various systems, the PET from the sacrificial electron donor, DMAEAc, to the PC was monitored through PL decay quenching experiments by transient PL measurement using the time-correlated single-photon counting technique. Considering the bulk polymerization conditions, ethyl acetate was used as a solvent for the photophysical studies. The 4-p,p-DCDP-IPN was excluded from this study owing to the aforementioned solubility issue. Under argon atmosphere, in the absence of DMAEAc, most of the PCs exhibited a PL with two components having approximately nanosecond and microsecond lifetimes (Figure 2a, inset). According to a previous report,^[77] the short and long components are assigned to prompt and delayed fluorescence, respectively, and the latter arises from a reverse intersystem crossing from the lowest T1 of the PC to its lowest singlet excited state (S1). Weak delayed fluorescence with a short decay time was observed for 4-o,p-DCDP-IPN, suggesting that the generation of long-lived T_1 is inefficient.

In the presence of DMAEAc, the lifetime of the delayed PL component of each of the PC was shortened (Figure 2b left and Figure S6, Supporting Information), suggesting that the T_1 of the PCs plays a critical role in the PET event. In fact, no quenching of the emission was observed for 4-*o*,*p*-DCDP-IPN even at a high DMAEAc concentration, because it has a negligible delayed component. Considering the excited-state

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and $E_{\rm red}$ *(T₁, 4Cz-IPN) = 1.47 V), the rate constant of PET was determined to increase with increasing $-\Delta G_{\rm PET}$, agreeing with the Marcus "normal region" behavior (Figure 2b and Figure S6, Supporting Information).^[76] Hence, the very small $k_{\rm PET}$ value of 4DP-IPN is due to its smallest $-\Delta G_{\rm PET}$.

As the rate of PET is determined by Equation (1), we attempted to estimate the effective excited-state concentrations of 4Cz-IPN, 4DP-IPN, and 4-*o*,*p*-DCDP-IPN. We modeled the time-dependent excited-state concentrations of the PCs under 455 nm irradiation based on the rate law using the rate constants obtained from our experiments (Figure 2c and Table S3, Supporting Information; see the Supporting Information for the details of the simulation and the rate equations employed). In the photostationary state, the relative T₁ concentrations of 4Cz-IPN and 4DP-IPN were found to be approximately 10 and 100 times higher than that of 4-*o*,*p*-DCDP-IPN, respectively. Indeed, the generation of long-lived T₁ in 4-*o*,*p*-DCDP-IPN was found to be significantly ineffective compared to that in 4Cz-IPN or 4DP-IPN, the reason for

which is currently under investigation. The results of these investigations adequately account for the best catalytic performance of 4Cz-IPN (i.e., a high excited-state population and moderate k_{PET}).

The PET from various amine reductants to 4Cz-IPN was monitored to investigate the effect of the amine-based additive on the polymerization of the BA/HBA mixture (Figure 2b right and Figure S7, Supporting Information). As expected, the PET was found to lie in a Marcus normal region. The slowest PET was observed for DMAEAc ($k_{\rm PET} = 2.1 \times 10^7 \text{ m}^{-1} \text{ s}^{-1}$ and E_{0x}^{0} (DMAEAc) = 0.96 V), which is clearly opposite to the observed high conversion in bulk polymerization. We thus hypothesize that the formation of α -amino radical species from the one-electron-oxidized amine reductant might be the rate-determining step instead of the initial PET event. To test this hypothesis, we calculated the free energy profiles along the reaction pathway for the formation of the α -amino radicals of DMAEAc and DIPEA (Figure 3a, lower part). Of the two possible reaction pathways (Figure 3a and Figure S10, Supporting Information), the one in which the proton-transfer is



Figure 3. a) Proposed mechanistic pathway for the formation of *α*-amino radical from radical cation of tertiary amines (top) and the density functional theory (DFT) calculated energy profiles of each pathways (bottom). b) Proposed mechanism of the oxygen-tolerance of bulk polymerizations in the presence of tertiary amines. The bond dissociation energies (BDEs) of C–H at the alpha position of DMAEAc and DIPEA are given.



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assisted by another amine required the lower activation energy (i.e., "path B").^[78–81] Furthermore, in path B, the formation of α -amino radical of DMAEAc exhibited a significantly lower activation barrier (10.15 kcal mol⁻¹) than that required for the formation of α -amino radical of DIPEA (22.49 kcal mol⁻¹), indicating that the α -amino radical generation is crucial for the entire photomediated polymerization process.

Finally, we investigated the role of oxygen in the bulk polymerization. The effect of oxygen in the bulk polymerization was found to be very sensitive to amines (Table 1). As stated above, tertiary amines are known to mitigate the oxygen-inhibition in photoinduced free radical polymerizations by converting inactive peroxyl radicals to reactive α -amino radical species.^[36] We thus calculated the bond dissociation energies (BDEs) for the α -hydrogen of DMAEAc and DIPEA. As seen in Figure 3b, DMAEAc exhibited a BDE of α -hydrogen (84.77 kcal mol⁻¹) that is higher than DIPEA (86.39 kcal mol⁻¹), which is consistent with the observed oxygen-effect. These results strongly suggest that the generation of α -amino radical species from a peroxyl radical is an essential step for achieving oxygen-tolerance. In addition, PCs also have a significant effect on oxygen-tolerance behavior. Indeed, a substantial decrease in PL lifetimes of PCs was detected in the presence of oxygen (Figure S8, Supporting Information), indicating that electron/energy transfer between ³PC* and oxygen is followed by the generation of reactive oxygen species such as singlet oxygen (¹O₂) (Figure S9, Supporting Information), superoxide radical anion (O_2^{\bullet}) , and hydroperoxyl radical. These reactive oxygen species could react with tertiary amine resulting in oxygen-tolerance behavior to keep the polymerization. For example, the generated superoxide radical anion (O_2^{\bullet}) can accelerate the initiation step by i) facilitating the formation of α -amino radical species^[82] and/or ii) generating reactive radical species such as hydroperoxyl radical (Figure 1b);^[83] in fact, our DFT calculations indicated that this pathway is feasible. However, it is very difficult to completely understand this behavior because of its complexity, and hence, further investigations are currently underway.

2.5. Film Curing

We further investigated the visible-light curing of the pre-polymer mixtures obtained by the bulk polymerization of the BA/HBA mixtures using the best combination of the PC and reductant, namely, 4Cz-IPN (10 ppm, Figure S11, Supporting Information) and DMAEAc (5000 ppm, Table S9, Supporting Information). Being different from the conventional UV-curing process, this process did not require additional photoinitiators because the PC is reused within the catalytic cycle of the pre-polymer preparation process. Moreover, a cross-linker such as poly(ethylene glycol) diacrylate (PEGDA) for the curing of films was not included in this process (which is discussed further below). The mixture obtained by the bulk polymerization was coated between two release films (silicone-treated 50 μ m-thick poly(ethylene terephthalate) film (PET_f), Youngwoo Trading) and then cured using a string-type LED (452 nm, 6 W, see SI for detail). The final thickness of the adhesive film was set to $\approx 50 \ \mu m$.

As in the bulk polymerization process, the film curing rates were found to be optimal at 10 ppm of 4Cz-IPN and 5000 ppm of DMAEAc, and 91.6% conversion was achieved in 3 min under 455 nm LED irradiation (Figure S12, Supporting Information). Unexpectedly, a significantly high gel content of 44.4% was observed even without the addition of PEGDA (Table 2). This is presumably because the hydroxybutyl moiety can participate in the cross-linking reaction in the presence of the PC and reductant, which occurs through a hydrogen atom transfer that is similar to that in the Norrish type || reaction.^[84] Indeed, film curing of the pre-polymer obtained for the bulk polymerization of BA did not show a gel content, clearly indicating that the hydroxy group plays a crucial role in the formation of crosslinks (Table S10, Supporting Information). Further comprehensive investigations are currently underway to fully understand the underlying mechanism.

These results indicated that substantial cross-linking could be achieved without the addition of cross-linker, but the degree of cross-linking was still insufficient to satisfy the mechanical and adhesive properties required for foldable OCAs. In fact, an OCA with a low degree of cross-linking is known to have a high peel strength owing to its good wettability,^[85] but it would exhibit low strain recovery because of the insufficient formation of the polymer network.^[86] In this study, to further increase the degree of cross-linking, we considered the use of DMAEA (or DMAEMA), a derivative of DMAEAc with an acryl (or methacryl) substituent on one end, instead of DMAEAc, based on the proposed mechanism of the photoredox-mediated visible light-driven free radical polymerization employed in the present study. As the iminium ion produced as an intermediate during the catalytic cycle can react with the hydroxyl group of HBA, DMAEA can act as a cross-linker owing to its bifunctional nature (see Figure in Table 2, bottom/right panel). Therefore, we employed a mixture of DMAEAc and DMAEA (or DMAEMA) as the hybrid reductant, while all other experimental conditions were maintained the same. As the OCA film curing rate was significantly faster with the use of DMAEA than with DMAEMA (Figure S12, Supporting Information), the DMAEAc/DMAEA mixture was found to be a better mixed reductant than DMAEAc/DMAEMA. As the proportion of DMAEA, which induces cross-linking, was increased, the gel content and strain recovery increased, and conversely, the peel strength and stress relaxation decreased (Table 2). A film with excellent peel strength, strain recovery, and stress relaxation was obtained at a DMAEA fraction of 40% or 60% in the mixture (Table 2, entries 3 and 4), and the properties of the OCAs prepared at these fractions were similar to those of the foldable OCA produced by 3M (CEF 3602).

The OCAs have been used to bond various substrates, including the cover window, within foldable displays. There are two types of cover windows for foldable displays: glass and colorless polyimide (CPI), and we assessed the peel strength of our OCA using these two substrates as adherends (Table 2). Glass is a much more hydrophilic substrate than CPI, and most OCAs, including CEF 3602, usually exhibit higher adhesion to hydrophilic substrates than to hydrophobic ones because of their differences in wettabilities.^[87] However, the prepared OCAs showed substantially higher peel strength to CPI than to glass, which has been rarely observed in



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Pre-polymer	$ \begin{array}{c} $	nm LEDs (6 W) or 30 min, r.t.		Crossl	inked polymer	
+ PC + unreacted	ÓН monomers / reductant		OCA film			
Proposed cross	linking mechanism: H-abstraction H-abstraction P_n-H	R = -Me (DMAR = -H (DMAR + Crosslinking)	H-a $H-a$ $H=MA$ H	$\xrightarrow{bstraction} H$ $0 (\xrightarrow{2} 0)$ $slinker 0$	$R \rightarrow 0 \rightarrow 1$	
 Reductant DMAEAc:DMAEA	Bulk polymerization conversion [%]	Gel content [%]	Peel strength at Glass	25 °C [N cm ⁻¹]	Strain recovery at 25 °C [%]	Stress relaxation at 25 °C(%)
100:0	21.8	44.4 (±3.1)	8.64 (±0.34)	8.39 (±0.77)	26.5	89.6
80:20	20.0	55.1 (±3.3)	6.85 (±0.57)	7.06 (±0.11)	54.1	69.5
60:40	20.7	68.6 (±4.8)	4.72 (±0.06)	6.83 (±0.18)	63.5	66.2
40:60	18.6	76.0 (±1.3)	4.20 (±0.05)	6.60 (±0.21)	79.7	54.8

4	40:60	18.6	76.0 (±1.3)	4.20 (±0.05)	6.60 (±0.21)	79.7	54.8
5	20:80	17.1	78.5 (±2.8)	3.60 (±0.07)	5.20 (±0.18)	83.1	47.9
6	0:100	20.8	82.1 (±1.3)	2.33 (±0.16)	3.93 (±0.46)	83.5	45.2
7 ^{a)}	60:40	16.1	72.7 (±1.0)	2.75 (±0.27)	5.42 (±0.50)	79.7	54.9
8 ^{a)}	40:60	19.3	72.9 (±1.3)	2.41 (±0.28)	5.37 (±0.26)	81.1	51.2
9	CEF 3602 (3M Foldable	e OCA)	64.0 (±1.1)	5.58 (±0.21)	1.94 (±0.04)	71.1	70.9

^{a)}Adding UV absorber after bulk polymerization.

Entry

1 2

3

conventional adhesives. In particular, the peel strength of the OCA prepared using the optimal content of DMAEA (40% or 60%) is three times higher than that of CEF 3602. The prepared OCA showed poor CPI peel strength at a short attachment time, but its peel strength was significantly improved with increasing attachment time (Figure S14, Supporting Information). Although the reason for this unusual increase in peel strength is still unclear, further investigations are currently underway.

2.6. UV-blocking OCAs

Next, we added a UV-absorber to the optimized OCA compositions (mixtures with 40% and 60% DMAEA) to produce the targeted UV-blocking OCAs. Among the various types of UV-absorbers, namely, benzotriazole, triazine, benzophenone, formamidine, and oxanilide,^[88] we used a cyanoacrylate-based UV-absorber with excellent compatibility with the acrylic monomers (ethyl 2-cyano-3,3-diphenylacrylate, UV-absorber 2 in Figure 4b). However, when UV-absorber 2 was used alone, only light wavelengths of less than 350 nm were blocked (Figure S15, Supporting Information). An additional UV-absorber was required to block light wavelengths from 350 to 400 nm (i.e., dimethyl 2-(4-(dimethylamino)benzylidene)malonate, UV-absorber 1 in Figure 4b). Therefore, two UV-absorbers, namely, 0.3 phr (per hundred resin) of UV-absorber 1 and 1 phr of UV-absorber 2, were added to the pre-polymer prepared through bulk polymerization, and UV-blocking OCAs were successfully prepared by curing the film using a blue LED. The resultant UV-blocking OCA exhibited excellent transmittance in the visible-light region ($T_{452 \text{ nm}} \approx 100\%$) while effectively blocking the UV-light $(T_{373 \text{ nm}} = 1.2\%$, Figure 4b). Such excellent transparency and UV-blocking ability have hardly been achieved together in

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Figure 4. a) Scheme for film curing of UV-blocking OCA. b) Chemical structure of UV-absorbers used in this work and UV-vis spectrum of the prepared UV-blocking OCA. Detailed information on the composition and preparation method is described in Figure S15, Supporting Information. c,d) Schematic illustration for procedure of dynamic folding test (c) and quantitative evaluation of folding durability (d). e) Results of dynamic folding experiments of UV-blocking OCAs. The structure of the specimen for the dynamic folding test is shown in Figure S16b, Supporting Information, and the UV-blocking OCAs in entries 7 and 8 in Table 2 were used for the experiments.

polyacrylate composites.^[89–91] Upon using a 452 nm blue LED, the curing time increased from 10 to 30 min according to the addition of the UV-absorbers, but it was significantly faster than when 373 nm light was used (Figure S15, Supporting Information). Although the peel strength of the OCA and stress relaxation decreased following the addition of the UV-absorbers, it still exhibited sufficiently decent peel strength (~5.4 and ~2.8 N cm⁻¹ on CPI and glass, respectively) and strain recovery (~80%) compared to those of CEF 3602 (Table 2).

We then conducted dynamic folding tests to verify whether the prepared UV-blocking OCAs are suitable for a foldable display (Figure 4c). The structure of the folding test specimen was designed with reference to the actual foldable smartphone (Figure S16, Supporting Information);^[30] the radius of curvature and the folding cycle were fixed at 1.5 mm and 0.5 Hz, respectively. To simulate the actual usage environment of a foldable smartphone, tests were conducted under three conditions: room temperature (25 °C for 200 000 cycles), low temperature (-20 °C for 30 000 cycles), and high temperature with high humidity (60 °C and 93% humidity for 50 000 cycles). Two specimens were tested at each condition, and the folding durability was evaluated quantitatively (i.e., change in surface texture after folding, Figure 4d) and qualitatively (i.e., occurrence of defects after folding, Figures S17 and S18, Supporting Information). Indeed, the prepared OCAs exhibited excellent folding durability even at a low temperature (Figure 4e), owing to their low storage modulus and high strain recovery at -20 °C (Tables S11 and S12, Supporting Information). As the testing temperature increased, the change in surface texture (ΔZ) was found to increase because of the reduction in the storage modulus. However, this would not generate significant problems because cracks were observed in only one specimen (at 25 °C folding with 40% DMAEA, Figure 4e and S18, Supporting Information). Interestingly, regardless of test conditions, UVblocking OCA containing 60% of DMAEA exhibited excellent folding durability, nearly satisfying the specifications for foldable displays. Nevertheless, by applying only a minimized SCIENCE NEWS _____ www.advancedsciencenews.com

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monomer composition and without using any functional additives such as those for improving the flexibility (Table S1, Supporting Information), we successfully produced UV-blocking OCAs that showed an excellent performance. In the future, superior UV-blocking OCAs of various grades may be prepared by employing a more complex composition with functional additives and monomers.

3. Conclusion

We have developed a novel and highly effective visible-lightcuring resin system to produce UV-blocking OCAs for foldable displays. Various photocatalysts and reductants with different properties were evaluated, and the combination of 4Cz-IPN and DMAEAc was determined to be the best for developing the UV-blocking OCA film. This mixture exhibited a fast photoinduced electron transfer rate that originated from excellent generation of triplet excited states and proper redox potentials, a facile generation of α -amino radical species, and a sufficient solubility in acrylic monomers, all of which helped to achieve the best curing performance with a strong oxygen-tolerance. After finding the best combination of the photocatalyst and reductant, we employed a mixed reductant system to finely control the cross-linking degree of the OCA. A mixture of DMAEAc and DMAEA was used as the hybrid reductant, and the OCA containing 40% or 60% of DMAEA had a suitable crosslinking degree and exhibited sufficient peel strength, strain recovery, and stress relaxation. Finally, by adding UV-absorbers to the optimized OCA composition, we successfully prepared UV-blocking OCAs that blocked wavelengths below 400 nm. The UV-blocking OCA containing 60% DMAEA exhibited excellent folding durability without any defects after dynamic folding tests under various conditions (25 °C, -20 °C, and 60 °C with 93% humidity), nearly satisfying the specifications for commercial foldable displays. Thus, a UV-blocking OCA was successfully prepared from two acrylic monomers using a limited number of additives (photocatalyst, reductant, and UV-absorber), and its potential can be improved further by adding other functional additives. Furthermore, the utility of the proposed visible light-curing system is not limited to the preparation of UV-blocking OCAs. It can also be applied to develop other systems such as optically clear resins, dental resins, and 3D/4D-printable materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

foldable displays, oxygen-tolerance, photocatalysts, UV-blocking adhesive, visible-light curing

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- [1] Y. Sun, J. A. Rogers, Adv. Mater. 2007, 19, 1897.
- [2] M.-C. Choi, Y. Kim, C.-S. Ha, Prog. Polym. Sci. 2008, 33, 581.
 [3] Y. Chen, J. Au, P. Kazlas, A. Ritenour, H. Gates, M. McCreary, Nature 2003, 423, 136.
- [4] T. R. Ray, J. Choi, A. J. Bandodkar, S. Krishnan, P. Gutruf, L. Tian, R. Ghaffari, J. A. Rogers, *Chem. Rev.* **2019**, *119*, 5461.
- [5] Y. Khan, A. E. Ostfeld, C. M. Lochner, A. Pierre, A. C. Arias, *Adv. Mater.* 2016, 28, 4373.
- [6] Y. Ma, Y. Zhang, S. Cai, Z. Han, X. Liu, F. Wang, Y. Cao, Z. Wang, H. Li, Y. Chen, X. Feng, Adv. Mater. 2020, 32, 1902062.
- [7] R. Feiner, T. Dvir, Nat. Rev. Mater. 2017, 3, 17076.
- [8] Y. J. Hong, H. Jeong, K. W. Cho, N. Lu, D. H. Kim, Adv. Funct. Mater. 2019, 29, 1808247.
- [9] D. Rus, M. T. Tolley, Nature 2015, 521, 467.
- [10] M. Wehner, R. L. Truby, D. J. Fitzgerald, B. Mosadegh, G. M. Whitesides, J. A. Lewis, R. J. Wood, *Nature* 2016, 536, 451.
- [11] C. Laschi, B. Mazzolai, M. Cianchetti, Sci. Rob. 2016, 1, eaah3690.
- [12] F. R. Fan, W. Tang, Z. L. Wang, Adv. Mater. 2016, 28, 4283.
- [13] H. Wu, Y. Huang, F. Xu, Y. Duan, Z. Yin, Adv. Mater. 2016, 28, 9881.
- [14] H. Sun, Y. Zhang, J. Zhang, X. Sun, H. Peng, Nat. Rev. Mater. 2017, 2, 17023.
- [15] M. M. Feldstein, E. E. Dormidontova, A. R. Khokhlov, Prog. Polym. Sci. 2015, 42, 79.
- [16] D. Satas, Handbook of Pressure Sensitive Adhesive Technology, Satas & Associates, Warwick, RI, USA 1999.
- [17] F. Salmon, A. Everaerts, C. Campbell, B. Pennington, B. Erdogan-Haug, G. Caldwell, SID Symp. Digest. Tech. Papers 2017, 48, 938.
- [18] G. F. Zapico, N. Takahara, K. Furuzono, R. Takahashi, F. Kawauchi, E. Ishikawa, Y. Mansei, T. Makino, *SIDSymp. Dig. Tech. Pap.* 2021, 52, 1321.
- [19] J. T. Abrahamson, H. Z. Beagi, F. Salmon, C. J. Campbell, in *Luminescence – OLED Technology and Applications*, IntechOpen, London, UK 2019.
- [20] Z. Han, A. Fina, Prog. Polym. Sci. 2011, 36, 914.
- [21] L. Ye, Z. Lai, J. Liu, A. Tholen, IEEE Trans. Electron. Packag. Manuf. 1999, 22, 299.
- [22] G. M. Taboada, K. Yang, M. J. Pereira, S. S. Liu, Y. Hu, J. M. Karp, N. Artzi, Y. Lee, *Nat. Rev. Mater.* **2020**, *5*, 310.

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- [23] P. J. Bouten, M. Zonjee, J. Bender, S. T. Yauw, H. van Goor, J. C. van Hest, R. Hoogenboom, *Prog. Polym. Sci.* 2014, *39*, 1375.
- [24] M. K. Kwak, H. E. Jeong, K. Y. Suh, Adv. Mater. 2011, 23, 3949.
- [25] M. A. Droesbeke, R. Aksakal, A. Simula, J. M. Asua, F. E. Du Prez, Prog. Polym. Sci. 2021, 117, 101396.
- [26] M. A. Hillmyer, W. B. Tolman, Acc. Chem. Res. 2014, 47, 2390.
- [27] L. A. Heinrich, Green Chem. 2019, 21, 1866.
- [28] Samsung Newsroom, Samsung Unfolds the Future with a Whole New Mobile Category: Introducing Galaxy Fold, http://bit. ly/2SD4yQY(accessed: February 2019).
- [29] H. E. Lee, D. Lee, T.-I. Lee, J. H. Shin, G.-M. Choi, C. Kim, S. H. Lee, J. H. Lee, Y. H. Kim, S.-M. Kang, S. H. Park, I.-S. Kang, T.-S. Kim, B.-S. Bae, K. J. Lee, *Nano Energy* **2019**, *55*, 454.
- [30] C. J. Campbell, J. Clapper, R. E. Behling, B. Erdogan, H. Z. Beagi, J. T. Abrahamson, A. I. Everaerts, *SID Symp. Digest. Tech. Papers* 2017, 48, 2009.
- [31] S. Kim, H.-J. Kwon, S. Lee, H. Shim, Y. Chun, W. Choi, J. Kwack, D. Han, M. Song, S. Kim, S. Mohammadi, I. Kee, S. Y. Lee, *Adv. Mater.* 2011, 23, 3511.
- [32] D. No, J. Kim, T. Kamine, H. Hwang (Samsung Display CO., Ltd.), US9444076B2, 2016.
- [33] R. E. Behling, J. D. Clapper, A. I. Everaerts, B. Erdogan-Haug (3M Innovative Properties Co.), WO2016196541A1, 2016.
- [34] G. Shah, Y. Liu (Henkel IP and Holding GmbH), WO2019133580A1, 2019.
- [35] K. Shitara, H. Ikenaga, H. Kishioka (Nitto Denko Corp.), US9580624B2, 2017.
- [36] S. C. Ligon, B. Husár, H. Wutzel, R. Holman, R. Liska, Chem. Rev. 2014, 114, 557.
- [37] C. Ollivier, P. Renaud, Chem. Rev. 2001, 101, 3415.
- [38] Z.-C. Zhang, T. M. Chung, Macromolecules 2006, 39, 5187.
- [39] D. Ahn, L. M. Stevens, K. Zhou, Z. A. Page, Adv. Mater. 2021, 33, 2104906.
- [40] C. E. Hoyle, C. N. Bowman, Angew. Chem., Int. Ed. 2010, 49, 1540.
- [41] L. Zhang, C. Wu, K. Jung, Y. H. Ng, C. Boyer, Angew. Chem., Int. Ed. 2019, 58, 16811.
- [42] C. Wu, K. Jung, Y. Ma, W. Liu, C. Boyer, Nat. Commun. 2021, 12, 478.
- [43] Y. Lee, Y. Kwon, Y. Kim, C. Yu, S. Feng, J. Park, J. Doh, R. Wannemacher, B. Koo, J. Gierschner, M. S. Kwon, *Adv. Mater.* 2022, 34, 2108446.
- [44] D. Jin, Z. Shi, X. Zhang, R. J. Petcavich (Unipixel Displays Inc), US20150267071A1, 2015.
- [45] J. L. Ferracane, Dent. Mater. 2011, 27, 29.
- [46] S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Chem. Rev. 2017, 117, 10212.
- [47] D. A. Nicewicz, D. W. MacMillan, Science 2008, 322, 77.
- [48] J. M. Narayanam, J. W. Tucker, C. R. Stephenson, J. Am. Chem. Soc. 2009, 131, 8756.
- [49] T. P. Yoon, M. A. Ischay, J. Du, Nat. Chem. 2010, 2, 527.
- [50] D. Konkolewicz, K. Schröder, J. Buback, S. Bernhard, K. Matyjaszewski, ACS Macro Lett. 2012, 1, 1219.
- [51] N. J. Treat, H. Sprafke, J. W. Kramer, P. G. Clark, B. E. Barton, J. Read de Alaniz, B. P. Fors, C. J. Hawker, *J. Am. Chem. Soc.* 2014, 136, 16096.
- [52] P. Xiao, J. Zhang, F. Dumur, M. A. Tehfe, F. Morlet-Savary, B. Graff, D. Gigmes, J. P. Fouassier, J. Lalevee, Prog. Polym. Sci. 2015, 41, 32.
- [53] S. Dadashi-Silab, S. Doran, Y. Yagci, Chem. Rev. 2016, 116, 10212.
- [54] J. C. Theriot, C.-H. Lim, H. Yang, M. D. Ryan, C. B. Musgrave, G. M. Miyake, *Science* 2016, 352, 1082.
- [55] N. Corrigan, S. Shanmugam, J. Xu, C. Boyer, Chem. Soc. Rev. 2016, 45, 6165.
- [56] N. Corrigan, J. Yeow, P. Judzewitsch, J. Xu, C. Boyer, Angew. Chem., Int. Ed. 2019, 58, 5170.
- [57] K. Jung, N. Corrigan, M. Ciftci, J. Xu, S. E. Seo, C. J. Hawker, C. Boyer, Adv. Mater. 2020, 32, 1903850.

- [58] X. Pan, C. Fang, M. Fantin, N. Malhotra, W. Y. So, L. A. Peteanu, A. A. Isse, A. Gennaro, P. Liu, K. Matyjaszewski, *J. Am. Chem. Soc.* 2016, *138*, 2411.
- [59] C. K. Prier, D. A. Rankic, D. W. MacMillan, Chem. Rev. 2013, 113, 5322.
- [60] N. A. Romero, D. A. Nicewicz, Chem. Rev. 2016, 116, 10075.
- [61] C. Wu, N. Corrigan, C.-H. Lim, W. Liu, G. Miyake, C. Boyer, Chem. Rev. 2022, 122, 5476.
- [62] M. Hayyan, M. A. Hashim, I. M. AlNashef, Chem. Rev. 2016, 116, 3029.
- [63] M. M. Islam, T. Ohsaka, J. Phys. Chem. C 2008, 112, 1269.
- [64] D. P. Hari, B. König, Org. Lett. 2011, 13, 3852.
- [65] M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny, D. C. Fabry, *Chem. Commun.* 2011, 47, 2360.
- [66] V. K. Singh, C. Yu, S. Badgujar, Y. Kim, Y. Kwon, D. Kim, J. Lee, T. Akhter, G. Thangavel, L. S. Park, J. Lee, P. C. Nandajan, R. Wannemacher, B. Milián-Medina, L. Lüer, K. S. Kim, J. Gierschner, M. S. Kwon, *Nat. Catal.* **2018**, *1*, 794.
- [67] Y. Song, Y. Kim, Y. Noh, V. K. Singh, S. K. Behera, A. Abudulimu, K. Chung, R. Wannemacher, J. Gierschner, L. Lüer, M. S. Kwon, *Macromolecules* **2019**, *52*, 5538.
- [68] J.-H. Back, Y. Kwon, H.-J. Kim, Y. Yu, W. Lee, M. S. Kwon, *Molecules* 2021, 26, 385.
- [69] J.-H. Back, Y. Kwon, J. C. Roldao, Y. Yu, H.-J. Kim, J. Gierschner, W. Lee, M. S. Kwon, Green Chem. 2020, 22, 8289.
- [70] J. Luo, J. Zhang, ACS Catal. 2016, 6, 873.
- [71] J. Lu, B. Pattengale, Q. Liu, S. Yang, W. Shi, S. Li, J. Huang, J. Zhang, J. Am. Chem. Soc. 2018, 140, 13719.
- [72] Y. Liu, X.-L. Chen, X.-Y. Li, S.-S. Zhu, S.-J. Li, Y. Song, L.-B. Qu, B. Yu, J. Am. Chem. Soc. 2020, 143, 964.
- [73] J. B. Sap, N. J. Straathof, T. Knauber, C. F. Meyer, M. Médebielle, L. Buglioni, C. Genicot, A. A. Trabanco, T. Noël, C. W. Am Ende, V. Gouverneur, J. Am. Chem. Soc. 2020, 142, 9181.
- [74] M. Garreau, F. Le Vaillant, J. Waser, Angew. Chem., Int. Ed. 2019, 58, 8182.
- [75] D. Anand, Z. Sun, L. Zhou, Org. Lett. 2020, 22, 2371.
- [76] T. P. Silverstein, J. Chem. Educ. 2012, 89, 1159.
- [77] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, 395, 151.
- [78] Y. Miyake, K. Nakajima, Y. Nishibayashi, J. Am. Chem. Soc. 2012, 134, 3338.
- [79] J. Hu, J. Wang, T. H. Nguyen, N. Zheng, Beilstein J. Org. Chem. 2013, 9, 1977.
- [80] P. J. DeLaive, T. K. Foreman, C. Giannotti, D. G. Whitten, J. Am. Chem. Soc. 1980, 102, 5627.
- [81] P. J. DeLaive, B. Sullivan, T. Meyer, D. Whitten, J. Am. Chem. Soc. 1979, 101, 4007.
- [82] Y. Pan, S. Wang, C. W. Kee, E. Dubuisson, Y. Yang, K. P. Loh, C.-H. Tan, Green Chem. 2011, 13, 3341.
- [83] P. S. Singh, D. H. Evans, J. Phys. Chem. B 2006, 110, 637.
- [84] N. Ballard, J. M. Asua, Prog. Polym. Sci. 2018, 79, 40.
- [85] S. D. Tobing, A. Klein, J. Appl. Polym. Sci. 2001, 79, 2230.
- [86] J.-H. Lee, T.-H. Lee, K.-S. Shim, J.-W. Park, H.-J. Kim, Y. Kim, S. Jung, Int. J. Adhes. Adhes. 2017, 74, 137.
- [87] A. Kowalski, Z. Czech, Int. J. Adhes. Adhes. 2015, 60, 9.
- [88] J. Pospišil, S. Nešpurek, Prog. Polym. Sci. 2000, 25, 1261.
- [89] J. Loste, J.-M. Lopez-Cuesta, L. Billon, H. Garay, M. Save, Prog. Polym. Sci. 2019, 89, 133.
- [90] Y. Zhang, X. Wang, Y. Liu, S. Song, D. Liu, J. Mater. Chem. 2012, 22, 11971.
- [91] H.-T. Liu, X.-F. Zeng, H. Zhao, J.-F. Chen, Ind. Eng. Chem. Res. 2012, 51, 6753.
- [92] C. Würth, M. Grabolle, J. Pauli, M. Spieles, U. Resch-Genger, Anal. Chem. 2011, 83, 3431.