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Solvent-free acrylic pressure-sensitive adhesives via a visible-light

driven photocatalytic radical polymerization without additives

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1. Supporting data

1.1. Steady-state photophysical properties of organic PCs (Eosin Y, 4Cz-IPN, and 4DP-IPN) and bulk polymerization results using those organic PCs



Figure S1. a) UV/Vis absorption (red) and photoluminescence (green) spectra of organic PCs. b) Results of bulk polymerization using Eosin Y and 4Cz-IPN. Conventional experimental conditions indicated in Table 1 of the manuscript were employed.

1.2. DFT calculation results of 4DP-IPN, NVP and MA



Figure S2. DFT calculated term scheme of 4DP-IPN (left), NVP (middle), and MA (right). For efficient energy transfer between a photocatalyst and a monomer, the lowest singlet/triplet state (S_1/T_1) energies of the photocatalyst should be similar or higher than those of the monomer. The S_1 and T_1 energies of 4DP-IPN (S_1 : 2.44 eV, T_1 : 2.24 eV) are much lower than those of NVP (S_1 : 5.33 eV, T_1 : 3.64 eV) and MA (S_1 : 4.90 eV, T_1 : 3.62 eV), which supports that initiation does not appear to occur through the energy transfer.



Figure S3. UV/Vis spectra were recorded from the sample taken before (gray) and after (red) bulk polymerization. The samples were prepared by dissolving the reaction mixture of bulk polymerization in ethyl acetate (5% v/v).

1.4. Preparation of acrylic PSA film via UV photo-initiator





Coating & film curing

Crosslinker (*PEGDA*, 1 wt%) Photo-initiator (Irgacure 184) 0.1 wt% Thickness: 120 μm Covered by release film *r.t.* [EHA]:[IBOA]:[AA]:[PI] = 65:30:5:0.045



+ Unreacted monomers

Irradiation time (s)	Conversion (%)
0	0
180**	78.6
600	97.8
	* UV intensity: 20 mW/cm ²

** Minimum irradiation time for film formation

Conversion (%)				
0				
12.0				
34.4				
52.2				
70.0				

* UV intensity: 300 mW/cm²

** Maximum conveyor speed for film formation

Figure S4. The film curing process and experimental conditions for the preparation of solvent-free acrylic PSA with conventional photoinitiator (i.e. Irgacure 184) was described. The monomer conversion was characterized for a) UV-light source with low power density (UV black light, ca. 20 mW/cm²) and b) with high power density (UV metal halide, ca. 300 mW/cm²).



1.5. Viscoelastic properties of acrylic PSAs with different NVP content

Figure S5. a) Frequency-storage modulus curve and b) viscoelastic window of acrylic PSAs with different NVP content. The irradiation time of blue LED for film curing was set as 60 min for all PSAs.

1.6. Mechanical and adhesive properties of PSAs with different NVP



Entry (Table 1 in manuscript)	Lap shear strength (MPa)	Elongation at break (mm/mm)	Peel strength (N/cm)	Loop tack (N/cm)
2	0.219	27.29	3.42	5.57
	(±0.033)	(±7.40)	(±0.10)	(±1.88)
5	0.249	39.83	3.30	5.20
	(±0.005)	(±1.75)	(±0.07)	(±0.69)
6	0.250	47.38	6.64	7.18
	(±0.007)	(±4.16)	(±0.38)	(±0.17)
7	0.254	52.93	7.48	6.34
	(±0.007)	(±3.90)	(±0.36)	(±1.09)
8	0.264	72.67	7.74	5.99
	(±0.012)	(±3.24)	(±0.20)	(±0.32)

Figure S6. 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. 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.



Figure S7. Differential scanning calorimetry results (sample; entries 1, 4, and 6 in Table 2 of the manuscript, sample weight; 9-10 mg, temperature step; Increasing (20°C/min, room temperature to 100°C, 1st scan) – Isothermal (3 min) – Decreasing (20°C/min, 100°C to -70°C) – Isothermal (3 min) – Increasing (5°C/min, -70°C to 40°C, 2nd scan), 2nd scan was shown).



Figure S8. a) Film curing process of solvent-free acrylic PSA. b) The film conversion (α_f) is plotted as a function of curing time for different photocatalyst content (entries 6, 11, and 12 in Table 1 of the manuscript).

2. Materials

Acrylic PSA was synthesized by incorporating several monomers; 2-ethylhexyl acrylate (EHA, 99%, Aldrich), isobornyl acrylate (IBA, 98.5%, Aldrich), and acrylic acid (AA, 99%, Aldrich). 4DP-IPN, 4Cz-IPN, eosin Y (99%, Aldrich) were used as photocatalyst. 4DP-IPN and 4Cz-IPN were synthesized and detail information on synthesis method was shown in references.^{1,2} Fig. S1 shows the UV/Vis absorption spectra and the photoluminescence intensity of the photo-catalysts. N-vinyl compounds including 1-vinyl-2-pyrrolidinone (99%, Junsei) and N-vinylcaprolactam (98%, Aldrich) were used as boosting monomer. Poly(ethylene glycol) diacrylate (Mn 700, Aldrich) was used as crosslinker. All monomers were purified by basic alumina in order to remove the inhibitor except acrylic acid which is purified by distillation.

3. Preparation of solvent-free acrylic PSA film

3.1. Bulk polymerization

As shown in Fig. S9, acrylic PSA film was prepared by two step; bulk polymerization and film curing. For bulk polymerization, monomer and photocatalyst were mixed and total volume of the mixture was set as 5 mL. The mixture was stirred (500 rpm) and degassed by purging Ar gas for 30 min, followed by it was exposed to visible light (1st irradiation) with bulb type LED (456 nm, 5 mW/cm², two bulbs). The irradiation time was differed by each samples for similar bulk conversion (about 10 %). Acrylic resin was synthesized by bulk polymerization and it consists of polymer chain and unreacted monomer. Bulk polymerization was conducted at constant temperature (23°C). For preparation of control sample, acrylate monomer was polymerized by photoinitiator (Irgacure 184, 0.05 wt.%) and UV light (365 nm, 3 mW/cm²).

3.2. Coating and film curing

The crosslinker (PEGDA) was added to the acrylic resin with constant content (1 wt.%), which was blended by paste mixer (mixing: 1700 rpm for 4 min/ defoaming: 1800 rpm for 2 min). It is not required to add photocatalyst because it is not consumable (see Fig. S3). The mixture was coated on the backing film, followed by a release film covered the surface in order to block atmospheric oxygen (final thickness of acrylic PSA film was set as 120 μ m). The coated mixture was exposed to visible light (2nd irradiation) by string type LED (448 nm, 0.3 mW/cm², three strings) for film curing. During the film curing, the unreacted monomer and the crosslinker reacted via photo-electron transfer reaction so that the acrylic PSA film was prepared (see Fig. S9).

[Step 2] Film curing



Figure S9. Preparation of solvent-free acrylic PSA via photocatalyst; step 1 (left, bulk polymerization) and step 2 (right, film curing).

4. Characterization

4.1. Size exclusion chromatography

After bulk polymerization, molecular weight and bulk conversion was evaluated by size exclusion chromatography (SEC, 1260 Infinity II LC, Agilent technologies). The synthesized polymers dissolve in tetrahydrofuran, not in N,N-dimethylformamide so that tetrahydrofuran (99.9% HPLC grade, Samchun) was used as eluent (flow rate: 1 mL min⁻¹). When we used fresh column that had clean surface, some of samples (entries 7, 8, and 10 in Table 1 of the manuscript & entry 1 in Table 2 of the manuscript) were not detected; it is assumed that the polymer incorporating high content of polar monomer (NVP and AA) absorbed onto the column. Therefore, we used an old column of which surface was fully absorbed by polar polymers. The temperature of the chamber was set as 40°C and signal was detected by reflex index detector (RID). All samples were calibrated by linear polystyrene.

4.2. Conversion (bulk polymerization)

Monomer conversion of bulk polymerization was estimated by using nuclear magnetic resonance (¹H-NMR, 300 MHz, Avance DPX-400, Bruker, solvent: CDCl₃). As shown in Fig. S10, peak intensity of protons from monomers (A_{mon}) decreased after bulk polymerization (A'_{mon}) with inert peak (A_{std} from EHA) as internal standard. Conversions of each monomers (α_{mon}) were calculated by following equation;

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

, where *A*_{mon}, *A*_{std}, *A*'_{mon}, *A*'_{std} means integration of representative peak from monomer before bulk polymerization, integration of standard peak before bulk polymerization, integration of representative peak from monomer after bulk polymerization, and integration of standard peak after bulk polymerization, respectively.

Total conversion (α_t) of bulk polymerization was calculated as follows;

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

, where x_{mon} represents mole fraction of each monomers.

a. 2-Ethylhexyl acrylate



Figure S10-1. ¹*H-NMR* spectra of monomers (a-e).



Figure S10-2. Example of ¹H-NMR spectra for calculation of monomer conversion of bulk polymerization: f) before and g) after bulk polymerization (EHA: 65 mol%, IBOA: 25 mol%, NVP: 5 mol%, AA: 5 mol%, 4DP-IPN: 50 ppm).

4.3. Conversion (film curing) & gel fraction

As PSA film was slightly crosslinked during the film curing, Fourier-transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Electron Corporation) was implemented in order to compare film conversion. Film conversion (α_f) was calculated by following equation;

$$\alpha_{f}(\%) = \frac{A_{0(C=C)} / A_{0(C=O)} - A_{t(C=C)} / A_{t(C=O)}}{A_{0(C=C)} / A_{0(C=O)}} \times 100$$

, where $A_{0(C=O)}$, $A_{t(C=O)}$, $A_{0(C=C)}$, and $A_{t(C=C)}$ represents C=O absorption peak area (1760-1660 cm⁻¹) at irradiation time 0 and t, C=C absorption peak area (830-795 cm⁻¹) at irradiation time 0 and t, respectively.



Figure S11. Evaluation of gel fraction of cured PSA.

Cured PSA consists of linear polymer and crosslinked polymer. Linear polymer is dissolved in toluene, while crosslinked polymer is not dissolved but swollen in toluene. As shown in Fig. S11, gel fraction can be evaluated by separating linear polymer and crosslinked polymer using a stainless steel mesh. Dissolved linear polymer passes through the mesh, but swollen crosslinked polymer cannot pass through the mesh. Gel fraction was calculated as follows:

Gel fraction (%) =
$$\frac{W_r}{W_t} \times 100$$

, where W_r and W_t represents weight of residue (crosslinked polymer) and total weight of cured PSA, respectively.

4.4. Dynamic mechanical analysis

Test specimen of viscoelasticity was prepared by following steps; The cured PSA film was laminated to have a thickness of 800 µm, followed by cut into specific area (10 mm X 10 mm). Viscoelasticity was characterized by using dynamic mechanical analysis (DMA, Q800, TA Instrument) with shear sandwich clamp. Testing mode was "DMA Multi-Frequency-Strain" and the strain was set as 1% to thickness of the specimens. Storage modulus, loss modulus were evaluated in the frequency range from 0.01 Hz to 100 Hz at constant temperature (23°C). DMA was conducted as single experiment.



Figure S12. Test scheme of dynamic mechanical analysis with shear sandwich clamp.

4.5. Single lap shear test

Mechanical property was evaluated by single lap shear test. Test specimen for single lap shear test was prepared as follows; The cured PSA film (length, width, thickness: 50 mm, 25 mm, 0.12 mm) attached to polyethylene terephthalate film (length, width, thickness: 50 mm, 25 mm, 0.05 mm) by constant force (2 kg roller, twice) with specific adhesion area (25 mm X 25 mm). Universal testing machine (UTM 5982, Instron) collected force values according to strain with constant testing speed (1 mm/s), Test specimen for single lap shear test was shown in Fig. S13a. From strain-stress curve of single lap shear test (Fig. S13b), maximum stress and maximum strain values were obtained, which represents lap shear strength and elongation at break, respectively. Tests were conducted at constant temperature (23°C) and repeated for 3 times.



Figure S13. a) Test specimen for single lap shear test and b) example of strain-stress curve of acrylic PSA (EHA: 65 mol%, IBOA: 20 mol%, NVP: 10 mol%, AA: 5 mol%, 4DP-IPN: 50 ppm).

4.6. 180° peel test

Adhesion properties were evaluated by both of 180° peel test and loop tack test. For 180° peel test, the acrylic PSA film (width = 10 mm) was attached on a substrate (steel: bright annealing treated SUS 304 / glass: sodalime-silica glass) by constant force (2 kg roller, twice). After 24 hours, debonding force was recorded by universal testing machine (UTM, LS1, Lloyd) with constant testing speed (5 mm/s, Fig. S14a). Peel strength was obtained by calculating the average of debonding force from 20% to 80% of working range (ASTM D3330, Fig. S14b). The tests were repeated for 3 times.



Figure S14. a) Test specimen for 180° peel test and b) example of extension-force curve of acrylic PSA (EHA: 65 mol%, IBOA: 20 mol%, NVP: 10 mol%, AA: 5 mol%, 4DP-IPN: 50 ppm).

4.7. Loop tack test

For loop tack test, the acrylic PSA film was cut into string with same width (10 mm) and length (150 mm). As shown in Fig. S15a, the string was bended as loop and it approach a substrate (steel: bright annealing treated SUS 304 / glass: soda-lime-silica glass) with constant cross-head speed (5 mm/s) until the distance between cross-head and the substrate became 25 mm. After that, the string was immediately detached from the substrate (5 mm/s) and the debonding force was collected by universal testing machine (UTM, LS1, Lloyd). From extension-force curve of the loop tack test, maximum force represents loop tack value (ASTM D6195, Fig. S15b). Tests were conducted at constant temperature (23°C) and repeated for 3 times.



Figure S15. a) Test procedure of loop tack test and b) example of extension-force curve of acrylic PSA (EHA: 65 mol%, IBOA: 20 mol%, NVP: 10 mol%, AA: 5 mol%, 4DP-IPN: 50 ppm).

5. Reproducibility test

Table S1. Reproducibility test results of bulk polymerization (see Table 1 and 2 in the manuscript). The values in blue boxes represent reproducibility test results conducted by another user. The values in yellow boxes are displayed in the manuscript.

	Reaction time (s)	α _t (%)	M _n (kg/mol)	Ð		Reaction time (s)	α _t (%)	M _n (kg/mol)	Ð
Entry 2 (Table 1)	320	7.53	897	1.54		185	12.14	172	2.98
	280	9.85	948	1.52	Entry 1	170	11.60	156	3.23
	260	6.45	967	1.52		160	11.40	162	3.03
	260	8.01	945	1.58		130	11.86	454	1.94
Entry 3 (Table 1)	15	18.23	379	2.04	Entry 2	130	11.65	336	1.95
	15	21.78	352	2.07		115	10.31	373	1.91
	13	17.64	350	2.09		140	10.08	498	1.85
	12	12.52	278	2.28	Entry 3 (Table 2)	115	9.11	512	1.78
	300	12.19	590	1.94		110	10.94	427	1.83
Entry 5 (Table 1)	220	11.27	709	1.74	Entry 4	135	9.30	701	1.72
	210	8.90	726	1.74		130	10.12	740	1.72
	210	9.16	622	1.54	(Table 2)	125	9.05	696	1.75
Entry 6	275	12.99	491	1.89		120	9.15	727	1.63
	145	10.56	655	1.64	Entry 5	115	8.68	573	1.69
	145	7.73	497	2.11	(Table 2)	110	8.87	476	1.71
(Table 1)	145	7.40	694	1.66		1290	8.67	1,167	1.51
	130	10.27	653	1.64	Entry 6	1273	9.44	1,075	1.61
	100	10.91	674	1.61	(Table 2)	1130	7.53	981	1.68
Entry 7	115	10.47	335	1.82		1030	13.11	897	1.79
	105	9.01	309	1.90					
(Table 1)	90	10.85	353	1.82					
	85	10.50	330	1.76]				
	70	10.38	154	2.15	1				
Entry 8	60	12.98	164	2.06]				
(Table 1)	60	13.40	143	2.32					
	53	12.66	154	2.07					
	600	10.23	563	1.75					
	520	9.53	510	1.65					
Entra de	360	8.97	628	1.69					
(Table 1)	250	10.12	629	1.63					
,	320	10.45	588	1.63					
	320	10.86	642	1.55					
	240	9.79	531	1.65					
Entry 12 (Table 1)	1575	14.85	559	2.07					
	1160	12.90	688	1.84					
	990	10.66	398	1.98					
	990	9.19	515	2.32					
	973	11.54	679	1.86					
	850	10.66	616	1.96					
Entry 13	125	7.27	647	1.69					
(Table 1)	170	9.07	560	1.81					

6. Calculations

Density functional theory (DFT) and time-dependent (TD) DFT calculations of 4DP-IPN and of NVP were performed with the B3LYP functional and the 6-311+G* basis set, in ethylethanoate solution, using the polarizable continuum model (PCM) as all implemented in the Gaussian16 program package.³ For 4DP-IPN, the calculations included geometry optimization (in the C₂ point group) of the electronic ground state (GS; S₀) and the first excited singlet and triplet states (S₁, T₁) of the neutral compound, GS geometries of the radical cation (RC) and radical anion (RA), adiabatic and vertical ionization potentials (IP) and electron affinities (EA), as well as the electronic structure (frontier MO energies ad topologies) in S₀. For NVP, geometries of the GS, RA and RC (all tautomers) were optimized, and adiabatic and vertical IP, EA were determined; Gibbs free energy calculations were done to determine the relative RC stabilities.

7. References

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