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Control of adhesive strength of acrylate polymers containing 1-isobutoxyethyl and isobornyl esters in response to dual stimuli for dismantlable adhesion

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Abstract

Background: To develop an adhesion system satisfying both constant adhesion strength during use and quick debonding ability during a dismantling process.

Methods: Adhesive properties were investigated for the random and block copolymers consisting of 1-isobutoxyethyl acrylate (iBEA), 2-ethylhexyl acrylate (2EHA), and 2-hydroxyethyl acrylate (HEA) as the dismantlable pressure-sensitive adhesives in the presence of a photoacid generator in response to dual external stimuli of photoirradiation and post baking.

Results: The use of LED combined with a new photoacid generator SIN-11 was enable us to achieve a rapid dismantling process during UV irradiation within several minutes. The protection of the ester alkyl group in the iBEA repeating unit to give an acrylic acid unit was suppressed by the introduction of isobornyl acrylate (IBoA) as the additional unit into the copolymer of iBEA, 2EHA, and HEA. While IBoA-containing block copolymer showed a constant adhesive strength during photoirradiation as the single external stimulus, deprotection was immediately induced by the subsequent heating, leading to a significant decrease in the adhesive strength.

Conclusion: The copolymer including the iBEA and IBoA units was revealed to function as the highly sensitive adhesive materials for dual-locked dismantlable adhesion.

Keywords: Pressure-sensitive adhesive, Polyacrylates, Reactive polymer, Photoacid generator, UV irradiation

Background

Dismantlable adhesion systems are smart technology and materials, which satisfy both a sufficient bonding strength during use and a quick debonding process on demand. They have attracted attention because of saving materials and energy in various application fields, such as housing, electronics, medical and dental applications as well as manufacturing processing for industrial parts and machines [1, 2]. For the design of dismantlable adhesive materials, the adhesive property needs to instantaneously change in response to any external stimulus as a trigger for dismantling, for example, heating, UV irradiation, induction heating, electricity, and chemicals [3–15]. A change in the chemical structures

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of the adhesives by external stimuli was expected to induce a significant change in the adhesive properties. We previously reported a dismantlable adhesive system using degradable polyperoxides as curable and pressure-sensitive adhesives and the control of bonding strength by the radical chain degradation of the polyperoxide adhesives [16–18]. More recently, we developed an advanced system using acrylic polymers containing *t*-butyl acrylate (tBA) unit in order to overcome the dilemma of reliable adhesion property during use and the subsequent quick debonding [19–24]. The tBA-containing polymers were demonstrated to function as the dismantlable adhesive materials due to a facile transformation to polymers including acrylic acid repeating units, accompanied by the elimination of isobutene gas, under the appropriate photo irradiation conditions followed by postbaking at a desired temperature. It was previously revealed that the tBA-containing block copolymers showed excellent dismantling properties compared with the corresponding random copolymers [19, 22]. The validity of the dual-locked adhesion system in the presence of a photoacid generator (PAG) was also reported. In this system, an acid was formed by the photoreaction of PAG, and then chemically amplified deprotection proceeded during postbaking, in which a large number of repeated chemical reactions were induced by a single photochemical event, resulting in the efficient transformation of protected functional groups.

In order to develop adhesives more sensitive to external stimuli, we investigated the dismantlable adhesion behavior of the acrylic copolymers consisting of 1-isobutoxyethyl acrylate (iBEA), 2-ethylhexyl acrylate (2EHA), and 2-hydroxyethyl acrylate (HEA) units [25]. Reactive polymers with functional groups protected with vinyl ethers have been synthesized and used for various applications, as reported in the literatures [26–31]. We found that the polymers containing the iBEA units were readily deprotected under single-stimulus conditions, such as hydrolysis without an acidic catalyst or acidolysis at room temperature under photoirradiation in the presence of PAG [25]. The use of the iBEA repeating unit as the reactive groups was suited to the construction of a quick debonding system, but the iBEA-containing copolymers were too reactive against the external stimuli such as heating in water and photoirradiation in the presence of PAG and consequently they were not applied as the dual-locked adhesive polymers. Previously, we reported that the deprotection conditions significantly depended on the stability of the ester groups of the adhesive polymers [19]. For example, the deprotection of the isobornyl ester proceeded under the conditions at a higher temperature for a longer reaction time in the presence of a larger amount of PAG. In this study, we investigated the dismantlable adhesion properties of the acrylic copolymers including an isobornyl acrylate (IBoA) unit in order to modify the responsibility of the iBEA-containing copolymers during a debonding process under the photoirradiation and subsequent heating conditions. We examined the dismantling properties of the random and block copolymers containing the iBEA, 2EHA, and HEA repeating units in the presence or absence of the additional IBoA repeating unit.

Experimental procedures

Measurements

The ^{1}H NMR spectra were recorded on a JEOL ECX-400 spectrometer using chloroform-*d* at room temperature. The number- and weight-average molecular weights (M_n

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and M_w) were determined by size exclusion chromatography (SEC) in tetrahydrofuran as the eluent at 40 °C using JASCO PU-2086 Plus equipped with UV-2075 Plus and 830-RIS detectors and Shodex A-800P columns. The molecular weights were calibrated with standard polystyrenes. The thermogravimetric (TG) and differential scanning calorimetry (DSC) were performed using Shimadzu DTG-60 and DSC-60, respectively, at a heating rate of 10 °C/min in a nitrogen stream. The 180° peel test was performed using a Shimadzu universal testing machine AGS-X with a 1 kN load cell according to ASTM D3330 at room temperature and a peel rate of 30 mm/min.

Materials

2EHA (Nacalai Tesque, Inc., Japan), HEA (Nacalai Tesque, Inc., Japan), and IBoA (Tokyo Chemical Industry Co., Ltd., Japan) were distilled under reduced pressure before use. 2,2′-Azobis(isobutyronitrile) (AIBN) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) were purchased from Wako Pure Chemicals Co., Ltd., Japan and recrystallized from methanol. Acrylic acid (Nacalai Tesque, Inc., Japan), isobutyl vinyl ether (Tokyo Chemical Industry Co., Ltd., Japan), 10-campharsulfonic acid (Tokyo Chemical Industry Co., Ltd., Japan), and diphenylditelluride (DPDT, Tokyo Chemical Industry Co., Ltd., Japan) were used as received. Other reagents and solvents were used without further purification. iBEA was synthesized according to the method described in the literature [25]. All copolymers were synthesized by organotellurium mediated radical polymerization (TERP) using binary azo initiators [20, 32]. SIN-11 [33–35] was supplied from Sanbo Chemical Industry, Ltd., Sakai, Japan, and used as received.
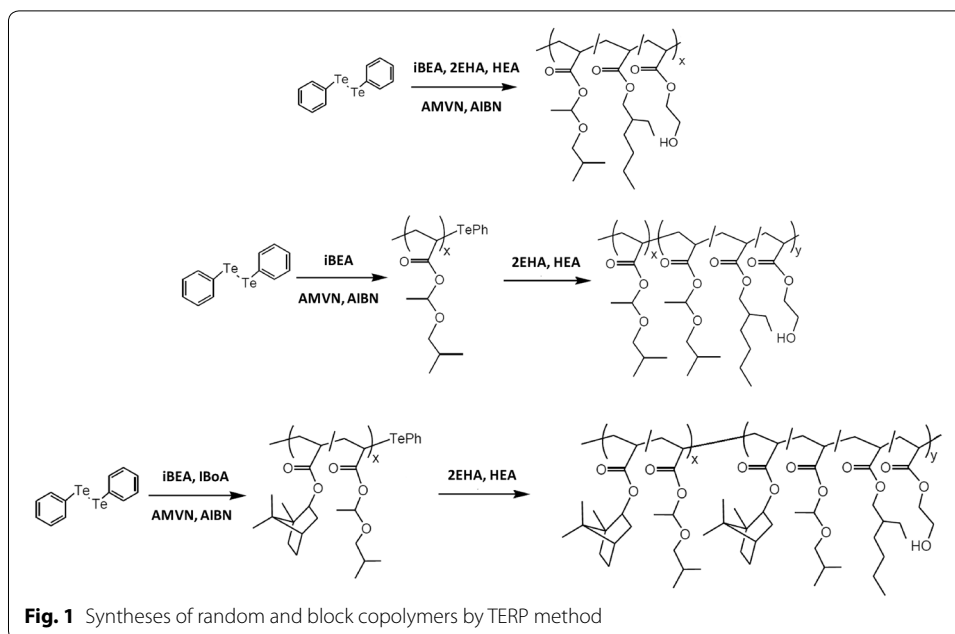
Synthesis of iBEA

To acrylic acid (17.98 g) and 10-campharsulfonic acid (6.0 mg) in 100 mL of *n*-hexane, isobutyl vinyl ether (25.28 g) was dropwise added at 0 °C under an argon atmosphere with stirring. After the addition, the stirring of a reaction mixture was maintained at room temperature for 3 h. Added was a small amount of calcium hydroxide then stirred for 30 min. After filtration, the solvent was removed under reduced pressure. The obtained crude product was distilled under reduced pressure. The pure iBEA was obtained in 97% yield.

iBEA

Liquid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.36 (dd, J = 17.4 and 1.5 Hz, C$\underline{H}_2$=CH (trans), 1H), 6.05 (dd, J = 17.4 and 10.5 Hz, CH$_2$=C$\underline{H}$, 1H), 5.92 (q, J = 5.4 Hz, OC$\underline{H}$(CH$_3$), 1H), 5.78 (dd, J = 10.5 and 1.5 Hz, C$\underline{H}_2$=CH (trans), 1H), 3.39 − 3.16 (m, OCH$_2$, 2H), 1.84-1.71 (m, CH$_2$C$\underline{H}$(CH$_3$)$_2$, 1H), 1.19 (d, J = 5.4 Hz, OCH(C$\underline{H}_3$), 3H), 0.82 (d, J = 6.6 Hz, CH(C$\underline{H}_3$)$_2$, 6H).

Synthesis of copolymers

A typical polymerization procedure was as follows [20] (Fig. 1). To a glass tube, iBEA (1.81 g), 2EHA (3.04 g), HEA (0.35 g), AIBN (1.6 mg), AMVN (3.5 mg), and DPDT (4.1 mg) in 1.38 g of anisole were added. The solution was degassed by a freeze–thaw technique three times, and then N$_2$ was purged. The polymerization was carried out at 60 °C for 7 h. The conversions of iBEA, 2EHA, and HEA were 52, 54, and 86%,

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Fig. 1 Syntheses of random and block copolymers by TERP method

respectively. The copolymer was separated using a methanol/water mixture (90/10 in volume ratio) as the precipitant. The yield was 1.79 g (37.8%). The M_n and M_w/M_n values were 1.41×10^5 and 1.59, respectively.

The block copolymers were synthesized according to the similar method [20] (Fig. 1). The homopolymerization of iBEA and the random copolymerization of iBEA and iBoA were carried out during the first stage of polymerization, and then 2EHA and HEA were further added to the polymerization systems to synthesize the corresponding block copolymers without isolating the precursor polymers produced at the first-step polymerization. To AIBN (1.6 mg), AMVN (3.5 mg), and DPDT (4.1 mg) in 1.5 g of anisole in a glass tube, was added 1.36 g of iBEA or a mixture of 0.95 g of iBEA and 0.62 g of IBoA. The solution was degassed by a freeze–thaw technique three times, and then N_2 was

Table 1 Synthesis of block copolymers by TERP

Code	First-step polymerization					Second-step polymerization		
	iBEA/IBoA[a]	Time (h)	Conversion of iBEA/IBoA (%)	$M_n/10^4$	M_w/M_n	2EHA/HEA[a]	Time (h)	Conversion of iBEA/IBoA/2EHA/HEA[b] (%)
B1	1050/0	9	58/–	2.3	1.16	1650/300	13	66/0/65/80
B2	600/300	22	59/25	3.1	1.31	2200/300	8	75/31/62/69

Polymerization conditions: [AMVN]/[AIBN] = 1.4/1.0 in the molar ratio to the DPDT and iBEA/anisole = 1/1 in weight at 60 °C. The homopolymerization of iBEA or the copolymerization of iBEA and IBoA was carried out during the first-step polymerization, and then 2EHA and HEA were added to synthesize the block copolymers during the second-step polymerization

[a] Molar ratio to DPDT

[b] The conversions for iBEA and IBoA indicate the total values of the first- and second-step polymerizations

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purged. After the polymerization was carried out at 60 °C for 9 or 22 h, the determined amount of 2EHA and HEA were added and the copolymerizations were continued in order to synthesize the corresponding block copolymers. The block copolymers were separated using a methanol/water mixture (90/10 in volume ratio) as the precipitant. The results of the copolymerization are summarized in Table 1.

180°peel tests

A SUS430 (150 × 50 × 0.5 mm³) plate was cleaned by ultrasonication in acetone for 15 min, then in 2-propanol for 15 min. The 15 wt% acetone solution of the polymer was applied on a poly(ethylene terephthalate) (PET) film (50 mm thickness) by a film applicator (200 μm gap). The film was dried in vacuo for 12 h in the dark, and then cut to a 20-mm wide. The film was pressure bonded on a SUS plate using a 2-kg hand roller. After UV irradiation (and the subsequent heating if needed), the 180° peel test was carried out after the specimen was left to stand for over 30 min at room temperature.
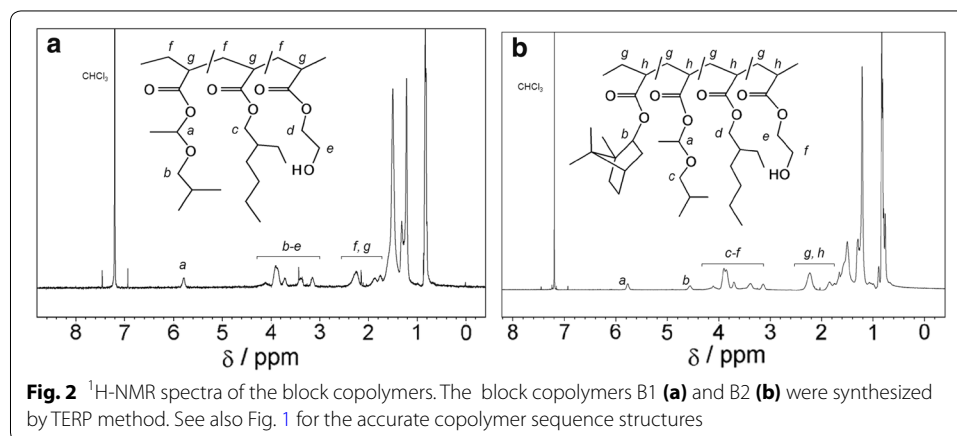
UV irradiation

UV irradiation was carried out using an LED lamp HLDL-50UV365-FN (365 nm, CCS Inc., Japan) at room temperature. For the UV irradiation, the test piece was placed at a distance in a range of 5.9–14.5 cm from the LED lamp. For the thermal treatment after the UV irradiation, the test piece was placed in a preheated oven for a determined time.

Table 2 Composition and property of random and block copolymers used in this study

Code	Composition in the copolymers (mol%)				IBoA content in the reactive segment[a] (mol%)	$M_n/10^4$	M_w/M_n	T_g (°C)
	iBEA	IBoA	2EHA	HEA				
R1	32	0	53	15	–	14.1	1.59	−19
B1	34	0	54	12	0	8.8	1.42	−54, −18
B2	21	5	64	10	17	10.8	1.74	−57, −18

[a] Determined based on the composition and conversion of each monomer for the reactive segment in the copolymers produced during the first-step polymerization. See Fig. 1 for the copolymer sequence structures

Fig. 2 ¹H-NMR spectra of the block copolymers. The block copolymers B1 **(a)** and B2 **(b)** were synthesized by TERP method. See also Fig. 1 for the accurate copolymer sequence structures

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Results and discussions

The random (polymer code R1) and block (B1 and B2) copolymers were synthesized using the TERP method as one of the living radical polymerization techniques. The results of the characterization of the obtained copolymers are summarized in Table 2. The structures of the obtained copolymers were determined based on the results of the NMR and SEC measurements, as shown in Fig. 2 and Table 2. The M_n values were high as $8.8–14.1 \times 10^4$ and enough for the use as the adhesive polymer materials. The copolymers included the reactive iBEA units in a range of 21–34 mol% while the content of the HEA unit was 10–15 mol%. The latter segment acts for enforcing the cohesive force of adhesives. The contents of the 2EHA repeating units as the major components were in a range of 53–64 mol%. The B1 and B2 copolymers included 0 and 5 mol% of the IBoA units, respectively. The IBoA content in the reactive segment was calculated to be 17 mol% for the B2 copolymer.
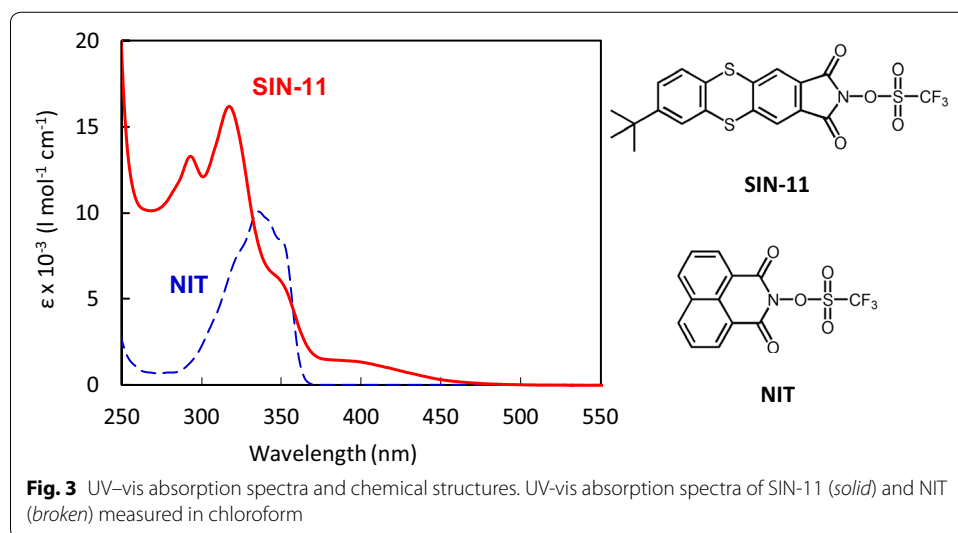
The T_g values of the homopolymers of iBEA, HEA, and IBoA were reported to be −10, −15, and 94 °C, respectively, being much higher than that of the homopolymer of 2EHA (−85 °C) [19, 25]. The T_g value was determined to be −19 °C for the random copolymer R1, which consisted of 2EHA unit (53 mol%) as the low T_g repeating unit and iBEA (32 mol%) and HEA (15 mol%) units as the moderate T_g repeating units. Because the introduction of IBoA into the copolymer increased the T_g values of the copolymers, we carefully controlled the copolymer compositions in order to exhibit similar T_g values for the copolymers with and without the IBoA unit. For the block copolymers synthesized in this study, the reactive segments showed the constant T_g values at −18 °C due to the small contribution of the IBoA unit introduced with an only 5 mol% into the reactive segment, as is shown in Table 2. The T_g values of the random copolymer R1 and the hard segment of the block copolymer B1 containing no IBoA unit were similar to each other. The effect of the M_n values (14.1×10^4 and 8.8×10^4 for R1 and B1, respectively) should be considered to discuss the T_g values of these copolymers. As a result, we successfully prepared three types copolymers containing a segment with T_g value. The adhesive segments consisting of 2HEA as the major component exhibited T_g values lower than −50 °C for the block copolymers. These T_g values were enough for the use as the pressure-sensitive adhesive materials. In this study, the adhesive segment including the mainly 2EHA units was produced during the second-step block copolymerization without isolation of the prepolymers produced during the first-step polymerization of iBEA or a mixture of iBEA and IBoA (See Fig. 1 for the accurate sequence structures of the block copolymers). Therefore, the second adhesive sequences produced during the second-step polymerization were confirmed to include not only the 2EHA and HEA repeating units but also small amounts of iBEA and IBoA repeating units as a result of the participation of the residual monomers after the first-step polymerization. The observation of two T_g values for the block copolymers (B1 and B2) undoubtedly indicated the microphase separation structure of the reactive segment produced during the first-step polymerization and the adhesive segment produced during the second-step polymerization.

In the previous study, we reported that the random copolymer consisting of iBEA, HEA, and 2EHA with the 73 mol% of iBEA contents readily deprotected and the drastic reduction of the adhesive strength was observed under the photoirradiation using

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N-hydroxynaphthalimide triflate (NIT) as the PAG and a high-pressure mercury lamp ($0.5–0.7$ mW/cm^2 at 330–390 nm) at room temperature [25]. NIT is one of the most popularly used i-line (365 nm) sensitive PAGs [34]. In this study, we used an LED lamp ($2–4$ mW/cm^2 at 365 nm) as the photoirradiation source and a new type of PAG, SIN-11 [34-36], which showed excellent optical properties as follows: $\lambda_{max} = 293$ and 317 nm, $\varepsilon_{max} = 1.35 \times 10^4$ and 1.62×10^4 L/mol cm, $\varepsilon_{365} = 2.45 \times 10^3$ L/mol cm. The ε_{365} value of SIN-11 was much higher than that of NIT ($\lambda_{max} = 335$ nm, $\varepsilon_{max} = 1.01 \times 10^4$ L/mol cm, $\varepsilon_{365} = 3.30 \times 10^2$ L/mol cm), as shown in Fig. 3.

First, the adhesion test was carried out using R1 as the random copolymer in the presence of SIN-11 (0.5 wt% against the polymer) under the irradiation intensity of 4 mW/cm^2 for 3 min (the irradiation dose was 720 mJ/cm^2). The relative value of the adhesion strength after photoirradiation was 1% of the original strength (Table 3). This indicated the validity of the copolymer containing a small amount of iBEA (32 mol%) for the quick dismantlable adhesion within a short time. We also investigated the effect of the polymer sequence structure on the dismantling behavior using the block copolymer (B1) under similar UV irradiation conditions for dismantling. As summarized in Table 3, quicker dismantling was achieved when the block copolymer was used. The 0.5-min irradiation (the irradiation dose 120 mJ/cm^2) of the block copolymer resulted in a decrease in the adhesive strength (0.042 ± 0.034 N/20 mm) similar to that after the 3-min irradiation (the irradiation dose 720 mJ/cm^2) of the random copolymer (0.035 ± 0.012 N/20 mm). As the previous results using the iBEA-containing adhesive polymers under the dismantling conditions in a hot water in the absence of an acid, the random copolymers provided preferred dismantling performance rather than the block copolymers [25]. The result obtained in this study was opposite to the previously reported one, being probably due to the difference in the dismantling conditions and the effects on the surface interactions, especially difference in the presence and absence of water.

Because the introduction of the IBoA unit was expected to suppress the deprotection, we tested the peel strength during the UV irradiation of the B2 copolymer, which consisted of the composition of the IBoA and iBEA units with 17/83 molar ratio in the

Fig. 3 UV–vis absorption spectra and chemical structures. UV-vis absorption spectra of SIN-11 (*solid*) and NIT (*broken*) measured in chloroform

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Table 3 Change in peel strength of random and block copolymers during photo irradiation using LED lamp

Code	Irradiation conditions			Post baking conditions	Peel strength (N/20 mm)	Relative value[a]	Failure mode
	Intensity (mW/cm²)	Time (min)	Dose (mJ/cm²)				
R1	0	0	0	None	2.65 ± 0.12	1	PET interface
	4	3.0	720	None	0.035 ± 0.012	0.01	SUS interface and cohesive (9/1)
B1	0	0	0	None	3.06 ± 0.06	1	Cohesive
	2	0.5	60	None	0.42 ± 0.11	0.13	Cohesive
	4	0.5	120	None	0.042 ± 0.034	<0.1	PET interface
	4	1.0	240	None	0.010 ± 0.003	<0.01	SUS and PET interfaces (5/5)
	4	3.0	720	None	0.0011 ± 0.00056	<0.01	SUS and PET interfaces (8/2)
B2	0	0	0	None	3.80 ± 1.27	1	SUS interface
	2	0.5	60	None	3.85 ± 0.06	1.0	SUS interface and cohesive (5/5)
	4	0.5	120	None	2.07 ± 0.16	0.54	SUS and PET interfaces (4/6)
	4	1.0	240	None	0.04 ± 0.008	<0.1	SUS and PET interfaces (9/1)
	4	3.0	720	None	0.11 ± 0.01	<0.1	PET interface
	2	0.5	60	3 min/100 ℃	0.079 ± 0.001	<0.1	PET interface
	4	0.5	120	3 min/100 ℃	0.057 ± 0.06	<0.1	PET interface

0.5 wt% of SIN-11 as PAG was added. Peeling rate was 30 mm/min

[a] The values of peel strength after treatment relative to before treatment

reactive segment. It should be noted that a copolymer with a higher IBoA content (ca. 30 mol%) exhibited poor adhesive property. The irradiation dose of 120 mJ/cm² was insufficient for the decrease in the adhesive strength for the test using B2 as the block copolymer containing the IBoA unit, while the same irradiation conditions were enough to significantly change the adhesive strength of the B1 sample. The fashion of a decrease in the adhesion strength as a function of the irradiation dose for the two kinds of block copolymers, B1 and B2, is shown in Fig. 4. The retardation of a decrease in the adhesion strength for B2 is clearly seen in this figure. We further investigated the postbaking effect of the B2 adhesives under the photoirradiation conditions at 60 and 120 mJ/cm². As a result, a drastic decrease in the adhesive strength was observed [Fig. 4(c)]. This result indicated that the block copolymer containing the IBoA units successfully acted as dual-locked adhesive polymers under the appropriate conditions used in this study, while the copolymers containing iBEA units were stable at 100 ℃ in dry conditions in the absence of an acid [25]. The chemically amplified reaction mechanism includes the photoirradiation process which produces a small amount of protons and the subsequent heating process which accelerates the deprotection reaction. This reaction mechanism is important for the dismantling adhesion system in response to the dual stimuli.

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Fig. 4 Change in peel strength. The peel strength of the block copolymers without and with IBoA units (B1 and B2, respectively) after UV irradiation using LED lamp: *(a)* B1 with no postbaking (*dash line*, *blue*), *(b)* B2 with no postbaking (*solid line*, *black*), and *(c)* B2 with postbaking at 100 °C for 3 min (*dot line*, *red*)
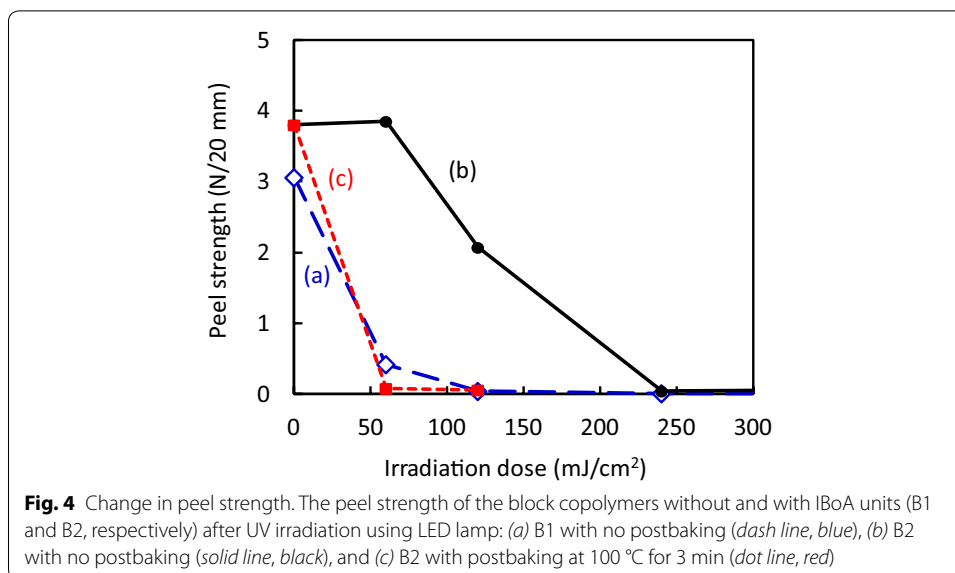
It was also found that the failure mode diversely changed depending on the photoirradiation conditions, as shown in Table 3. For the failure mode of the copolymers with different sequence structures, i.e., R1 and B1, the mode for the both copolymers changed depending on the photoirradiation dose as follows: cohesive failure, failure at the PET/adhesive interface, and then failure at the SUS/adhesive and PET/adhesive interfaces. In the case of R1, the failure occurred at the PET interface due to the considerably high cohesive force rather than the PET/adhesive interface interaction. The high molecular weight of R1 was favorable for increasing the cohesive interaction. The cohesive force further increased along with the photoirradiation because of the formation of polar and functional groups as well as the occurrence of cross-linking. The interactions at the SUS/adhesive and PET/adhesive interfaces competed with each other and determined the failure mode, but the both interactions seemed to be weak and finally the isolation of the adhesive layers was often observed. In fact, it was considered that the transesterification and/or esterification of the HEA unit took place with the deprotection of the iBEA unit in the presence of an acid catalyst causing cross-linking [24]. In the previous study, the adhesive layer stuck on the PET film was easily peeled off and consequently the cross-linked adhesive layer was removed from both the SUS and PET without any adhesive deposit [25]. The cross-linking caused by the reactions of the HEA units temporarily increased the modulus of the adhesives. In this study, the SUS or PET interface failure observed after dismantling was accounted for by similar cross-linking and transesterification reactions. The heating process for the dismantling using dual external stimuli led to the interfacial failure between the PET and adhesives because of an increase in the interaction between the SUS surface and the adhesives containing a carboxylic acid. However, it was hard to fully explain the all failure modes of B2 including hydrophobic IBoA, hydrophilic HEA, and reactive iBEA units as well as adhesive 2EHA unit under various irradiation and heating conditions for dismantling, because they kaleidoscopically changed according to the dismantling conditions.

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Conclusions

We synthesized the random and block copolymers consisting of iBEA, 2HEA, and HEA repeating units in the absence and presence of IBoA by the TERP method as the living radical polymerization technique, which was valid for the synthesis of high-molecular-weight acrylate polymers including polar and functional groups in the side chain. The adhesion property of the obtained iBEA copolymers were investigated as the dismantlable adhesives responsible to photoirradiation and heating. It was demonstrated that the use of LED combined with a new photoacid generator SIN-11 was enable us to achieve a rapid dismantling process during UV irradiation within several minutes. The introduction of the IBoA unit into the copolymer resulted in the enhanced resistance to photoirradiation, while the subsequent heating at 100 °C for 3 min immediately led to a significant decrease in the adhesion strength. Thus, the copolymer including the iBEA and IBoA units was revealed to successfully function as the highly sensitive adhesive materials for dual-locked dismantlable adhesion.

References
1. Sato C. Recent trends of dismantlable adhesives. J Jpn Soc Colour Mater. 2014;87:245–9.
2. Matsumoto A. Studies on the synthesis of degradable polymers by radical polymerization and the design of dismantlable adhesion materials. J Adhes Soc Jpn. 2014;50:72–81.
3. Boyne JM, Millan EJ, Webster I. Peeling performance of a novel light switchable pressure-sensitive adhesive. Int J Adhes Adhes. 2001;21:49–53.
4. Ebe K, Seno H, Horigome K. UV curable pressure-sensitive adhesives for fabricating semiconductors. I. Development of easily peelable dicing tapes. J Appl Polym Sci. 2003;90:436–41.
5. Nishiyama Y, Uto N, Sato C, Sakurai H. Dismantlement behavior and strength of dismantlable adhesive including thermally expansive particles. Int J Adhes Adhes. 2003;23:377–82.
6. Trenor SR, Long TE, Love BJ. Development of a light-deactivatable PSA via photodimerization. J Adhes. 2005;81:213–29.
7. Ishikawa H, Seto K, Shimotuma S, Kishi N, Sato C. Bond strength and disbonding behavior of elastomer and emulsion-type dismantlable adhesives used for building materials. Int J Adhes Adhes. 2005;25:193–9.
8. Leijonmarck S, Cornell A, Danielsson C-O, Lindbergh G. Electrochemical characterization of electrically induced adhesive debonding. J Electrochem Soc. 2011;158:109–14.
9. Kobayashi M, Takahara A. Environmentally friendly repeatable adhesion using a sulfobetaine-type polyzwitterion brush. Polym Chem. 2013;4:4987–92.
10. Akiyama H, Kanazawa S, Okuyama Y, Yoshida M, Kihara H, Nagai H, Norikane Y, Azumi R. Photochemically reversible liquefaction and solidification of multiazobenzene sugar-alcohol derivatives and application to reworkable adhesives. ACS Appl Mater Interfaces. 2014;6:7933–41.
11. Heinzmann C, Salz U, Moszner N, Fiore GL, Weder C. Supramolecular cross-links in poly(alkyl methacrylate) copolymers and their impact on the mechanical and reversible adhesive properties. ACS Appl Mater Interfaces. 2015;7:13395–404.
12. Suyama K, Tachi H. Photo-induced decrosslinking in pressure-sensitive adhesives composed of O-acyloxime-based photolabile crosslinkers. J Photopolym Sci Technol. 2015;28:45–8.
13. Wang YZ, Li L, Du FS, Li ZC. A facile approach to catechol containing UV dismantlable adhesives. Polymer. 2015;68:270–8.
14. Higashihara T, Fu MC, Uno T, Ueda M. Synthesis and characterization of polycyanurates as dismantlable adhesives. J Polym Sci, Part A: Polym Chem. 2016;54:1153–8.

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15. Sasaki T, Hashimoto S, Nogami N, Sugiyama Y, Mori M, Naka Y, Le KV. Dismantlable thermosetting adhesives composed of a cross-linkable poly(olefin sulfone) with a photobase generator. ACS Appl Mater Interfaces. 2016;8:5580–5.
16. Sato E, Matsumoto A. Facile synthesis of functional polyperoxides by radical alternating copolymerization of 1,3-dienes with oxygen. Chem Rec. 2009;9:247–57.
17. Sato E, Tamura H, Matsumoto A. Cohesive force change induced by polyperoxide degradation for application to dismantlable adhesion. ACS Appl Mater Interfaces. 2010;2:2594–601.
18. Sato E, Hagihara T, Matsumoto A. Facile synthesis of main-chain degradable block copolymers for performance enhanced dismantlable adhesion. ACS Appl Mater Interfaces. 2012;4:2057–64.
19. Inui T, Sato E, Matsumoto A. Pressure-sensitive adhesion system using acrylate block copolymers in response to photoirradiation and postbaking as the dual external stimuli for on-demand dismantling. ACS Appl Mater Interfaces. 2012;4:2124–32.
20. Inui T, Yamanishi K, Sato E, Matsumoto A. Organotellurium-mediated living radical polymerization (TERP) of acrylates using ditelluride compounds and binary azo initiators for the synthesis of high-performance adhesive block copolymers for on-demand dismantlable adhesion. Macromolecules. 2013;46:8111–20.
21. Yamanishi K, Sato E, Matsumoto A. Precise synthesis of acrylic block copolymers and application to on-demand dismantlable adhesion systems in response to photoirradiation and postbaking. J Photopolym Sci Technol. 2013;26:239–44.
22. Inui T, Sato E, Matsumoto A. High-molecular-weight and polar acrylate block copolymers as high-performance dismantlable adhesive materials in response to photoirradiation and postbaking. RSC Adv. 2014;4:24719–28.
23. Sato E, Taniguchi K, Inui T, Yamanishi K, Horibe H, Matsumoto A. Dismantling behavior of pressure sensitive adhesives using acrylic block and random copolymers in response to photoirradiation and postbaking. J Photopolym Sci Technol. 2014;27:531–4.
24. Sato E, Iki S, Yamanishi K, Horibe H, Matsumoto A. Dismantlable adhesion properties of reactive acrylic copolymers resulting from cross-linking and gas evolution. J Adhesion. 2016. doi:10.1080/00218464.2016.1209114.
25. Sato E, Yamanishi K, Inui T, Horibe H, Matsumoto A. Acetal-protected acrylic copolymers for dismantlable adhesives achieving spontaneous and complete removal of adhesives. Polymer. 2015;64:260–7.
26. Taylor GN, Stillwagon LE, Houlihan FM, Wolf TM, Sogah DY, Hertler WR. Positive, chemically-amplified aromatic methacrylate resist employing the tetrahydropyranyl protecting group. Chem Mater. 1991;3:1031–40.
27. Hertler WR, Sogah DY, Raymond FA, Bauer RD, Chang CT, Taylor GN, Stillwagon LE. Synthesis and applications of acid-labile acrylic polymers. Makromol Chem, Macromol Symp. 1992;64:137–49.
28. Simmons HE III, Hertler WR, Sauer BB. Phototackification of polymer blends. J Appl Polym Sci. 1994;52:727–35.
29. Malik S, Blakeney AJ, Ferreira L, Maxwell B, Van Driessche V, Whewell A, Sarubbi TR, Bowden MJ, Fujimori T, Tan S, Aoai T, Uenishi K, Kawabe Y, Kokubo T. Recent advances in acetal-based BUY resists. J Photopolym Sci Technol. 1999;12:591–600.
30. Nakane Y, Ishidoya M, Endo T. Synthesis and thermal dissociation of polymers having hemiacetal ester moieties. J Polym Sci, Part A: Polym Chem. 1999;37:609–14.
31. Wouters D, Van Camp W, Dervaux B, Du Prez FE, Schubert US. Morphological transition during the thermal deprotection of poly(isobornyl acrylate)-b-poly(1-ethoxyethyl acrylate). Soft Matter. 2007;3:1537–41.
32. Yamago S, Iida K, Nakajima M, Yoshida J. Practical protocols for organotellurium-mediated living radical polymerization by in situ generated initiators from AIBN and ditellurides. Macromolecules. 2003;36:3793–6.
33. Okamura H, Naito H, Shirai M. I-line sensitive non-ionic photoacid generators having thianthrene skeleton. J Photopolym Sci Technol. 2008;21:285–8.
34. Okamura H, Shirai M. I-line sensitive photoacid generators Trends Photochem Photobio. 2013;15:51–61.
35. Fukamoto Y, Ashida T, Okamura H, Sato E, Horibe H, Matsumoto A. Design of debonding processes for quick dismantlable adhesion system. J Adhes Soc Jpn. 2016;52:198–207.