Design of a High-Performance Dismantlable Adhesion System Using Pressure-Sensitive Adhesive Copolymers of 2-Hydroxyethyl Acrylate Protected with tert-Butoxycarbonyl Group in the Presence of Cross-Linker and Lewis Acid

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Supporting Information

ABSTRACT: A dismantlable adhesion system satisfies both a strong bonding strength during use and a quick debonding process on demand in response to an external stimulus as a trigger for dismantling. In this study, we synthesized acrylate copolymers consisting of 2-((tert-butoxycarbonyloxy)ethyl acrylate (BHEA), 2-ethylhexyl acrylate (2EHA), and 2-hydroxyethyl acrylate (HEA) as the repeating units and evaluated the properties as dismantlable adhesives. First, the thermal degradation behavior of the obtained polymers was investigated by thermogravimetric analysis and IR spectroscopy. The BHEA-containing polymers were thermally stable during heating at a temperature below 150 °C, but they rapidly degraded, i.e., the deprotection of the tert-butoxycarbonyl groups occurred during heating at 200 °C. The onset temperatures for the deprotection depended on the BHEA and HEA contents and their sequence structures because the hydroxy group in the side chain accelerated the deprotection via an autocatalytic reaction mechanism. Shear holding power and 180° peel tests were carried out with the pressure-sensitive adhesive tapes using the BHEA-containing copolymers as the adhesive materials. The copolymers consisting of the BHEA, 2EHA, and HEA units with 25.7, 35.0, and 39.3 mol %, respectively, exhibited the highest adhesion strength and the subsequent quick reduction of the adhesion strength by heating during the dismantling process. The addition of hexamethylene diisocyanate as the cross-linker and Zn(acac)2 as the Lewis acid to the adhesive polymers was demonstrated to be valid for the design of high-performance dismantlable adhesion systems. A change in the rheological properties during the dismantling process was important for a quick response and selective interfacial failure between the substrate and the adhesive.

INTRODUCTION

Recently, adhesion science and technology have become more important in interdisciplinary fields.1 In fact, adhesion bonding is indispensable for the construction of new multimaterial systems consisting of metals, ceramics, thermoplastic polymers, thermosetting resins, fiber-reinforced plastics, and bio-related materials as the composites.2−7 A dismantlable (i.e., on-demand debonding) adhesion system, which implies both a strong bonding strength without deterioration during use and a demand debonding) adhesion system, which implies both a strong bonding strength without deterioration during use and a quick reduction in the bonding strength on demand, is smart technology for the fields of material recycling and temporary bonding.8 For the design of dismantlable adhesive materials, their adhesive properties are required to instantaneously change in response to any external stimulus as a trigger for dismantling. In recent decades, various adhesive materials and their dismantling systems have been reported, i.e., photoswitchable polymers,9−13 chemically and photodegradable polymers,14−21 thermally expansive microcapsules,22,23 electro-chemically reactive systems,24,25 polyelectrolyte brushes,26 reversible cross-linking,27−30 supramolecular polymers,31,32 bioinspired systems,33−36 etc.

We previously reported dismantlable adhesion systems using reactive acrylic copolymers consisting of tert-butyl acrylate (tBA), 2-ethylhexyl acrylate (2EHA), and 2-hydroxyethyl acrylate (HEA) units as the pressure-sensitive adhesive polymers.37−39 A photoacid generator was used to simultaneously obtain thermal stability during use and high reactivity for the debonding after acid generation by photoirradiation.37 In this system, the significant reduction of the peel strength was achieved by the acid-catalyzed depolymerization of the tBA units in the copolymers after applying dual stimuli, i.e., photoirradiation with subsequent heating. To design adhesives...
more sensitive to external stimuli, we developed acrylic copolymers containing the 1-isobutoxyethyl acrylate unit, which were readily deprotected under single-stimulus conditions, such as hydrolysis and acidolysis at room temperature under photoirradiation. These adhesion systems were highly sensitive to an acid catalyst. Therefore, a lack of stability during storage for a long time or against an unexpected heating in the presence of any acidic compound was disadvantageous for application uses in various fields.

As one of the other protecting groups, the tert-butoxycarbonyl (BOC) group has been used for chemically amplified photoresists and programmed degradation of polymeric materials because tert-butoxycarbonyloxybenzenes are quantitatively transformed into the corresponding phenols accompanying the evolution of carbon dioxide and isobutene gases. The thermally induced and acid-catalyzed degradation behavior of poly(4-(tert-butoxycarbonyloxy)styrene) (PBSt) has been intensively investigated. We also reported the thermal degradation and gas bubbles formation of the polymers including a BOC group in the side chain. The deprotection of the BOC groups was expected to be applied to the design of pressure-sensitive adhesive polymers, but no report about the synthesis and application of polycrylates including BOC groups was found in the literature, except the thermal degradation of poly(4-(tert-butoxycarbonyloxy)phenyl)methyl acrylate. This acrylate polymer including the BOC-protected phenyl moiety exhibited a thermal degradation behavior similar to that of PBST. The polymers containing the BOC-protected phenyl moiety are sensitive to thermal and acidic stimuli and useful as reactive polymers, such as resist materials. On the other hand, both the robustness during use and the quick response for dismantling are needed for the practical use of dismantlable adhesives. In addition, selective interface failure without any pollution of the substrates by the adhesive transfer is also required by the adhesive materials. The addition effects of the diisocyanate and isobutene as gaseous products upon heating 43 group has been used for chemi- fields.

RESULTS AND DISCUSSION

Synthesis of BHEA-Containing Polymers. BHEA was prepared by the reaction of HEA with tert-butyl dicarbonate by stirring in toluene at room temperature for 24 h in the presence of 4-dimethylaminopyridine (DMAP), as shown in Scheme 1. BHEA was isolated as a colorless liquid in 87% yield. The radical polymerization of BHEA in the absence and presence of 2EHA and HEA was carried out in anisole at 60 °C with 2,2′-azobis(isobutyronitrile) (AIBN) to synthesize the homopolymer of BHEA (P1), the copolymers of BHEA with 2EHA (P2s), and the copolymers of BHEA with 2EHA and HEA (P3s), as shown in Scheme 2. The results for the synthesis of the polymers are summarized in Table 1.

After 3 h polymerization, the polymers were isolated in 41–90% yields by precipitation in a large amount of a methanol/water mixture in 9/1 volume ratio. The obtained polymers were soluble in chloroform and tetrahydrofuran (THF), and they were used for NMR and size exclusion chromatography (SEC) measurements. P3c containing the highest amount of HEA (54.6 mol %) was exceptionally insoluble in THF. The Mw values were as high as 1.5–6.3 × 10^5, being sufficient to function as adhesive polymers. The ^1H NMR spectra of the obtained polymers are shown in Figure S1. The copolymer compositions were determined based on the intensity ratio of the characteristic methylene peaks, i.e., −OCH2CH2O− for the BHEA unit observed at 4.2 ppm, −OCH2− for the 2EHA unit at 3.9 ppm, and −CH2OH for the HEA unit at 3.8 ppm. During the copolymerization of BHEA and 2EHA, the copolymer compositions were almost the same as the composition in the feed, due to the similar copolymerization reactivities of BHEA and 2EHA. For the three-component copolymerization, including BHEA, 2EHA, and HEA, a larger amount of HEA and a smaller amount of BHEA were incorporated into the copolymers, due to the high reactivity of HEA. It was reported that HEA showed a reactivity higher than 2EHA during radical copolymerizations, i.e., r1 = 0.88 and r2 = 0.5 for the copolymerization of HEA (M1) and ethyl acrylate (M2), r1 = 0.43 and r2 = 0.28 for the copolymerization of HEA (M1) and styrene (M2), and r1 = 0.23 and r2 = 1.17 for the copolymerization of ethyl acrylate (M1) and styrene (M2) in the literature. Recently, the enhanced reactivity of the vinyl monomers by the interaction with hydroxy groups during the radical polymerization has been revealed by various approaches, such as kinetic analysis, solvent effect, density functional theory calculations, and radical polymerization of vinyl ethers, etc.

The glass-transition temperature (Tg) of P1 was determined to be 20.0 °C by differential scanning calorimetry (DSC) measurement. For the copolymers with 2EHA, P2s, the Tg value decreased along with an increase in the 2EHA content to −64.1 °C. The three-component copolymers, P3s, had Tg values in the range of −18.0 to −26.6 °C, corresponding to the content of 2EHA (28.4–48.2 mol %). These Tg values suggest the availability of these copolymers as pressure-sensitive adhesive materials.

Thermogravimetric (TG) Analysis. The thermal stability of the BHEA-containing polymers was investigated by thermogravimetric (TG) analysis at a heating rate of 10 °C/min in nitrogen stream. The thermograms for P1, P2c, and P3b are shown in Figure 1. The BOC group released carbon dioxide and isobutene as gaseous products upon heating around 200 °C, as shown in Scheme 3. The Tds and Tmax values for the first-step reaction as the deprotection of a BOC group and those for the second-step degradation of the deprotected polymers are summarized in Table 2.

Scheme 1. Synthesis of BHEA
observed and theoretical residual weights are also shown in Table 2.

The \(T_d\) and \(T_{\text{max}}\) values for the deprotection of P1 were 199 and 215 °C, respectively. The residual weight after the first step deprotection was 53.3%, which well agreed with the calculated value (53.7%). For the copolymers of BHEA with 2EHA (P2a–e), the \(T_d\) and \(T_{\text{max}}\) values increased with an increase in the 2EHA content. The degradation temperatures were 239 and 243 °C for the BOC groups included in P2e, of which the 2EHA content was 89.4 mol %. For the copolymers of BHEA with 2EHA and HEA (P3a–c), the \(T_d\) values were in the range of 170–194 °C and the \(T_{\text{max}}\) values were in the range of 208–226 °C. For the copolymer preparation in this study, we fixed the BHEA and 2EHA contents at a 1/1 molar ratio in the feed to keep the appropriate \(T_g\) value for the pressure-sensitive adhesive materials. As a result, each content in the copolymers varied according to their copolymerization reactivity (see Table 1). The degradation temperatures decreased along with an increase in the HEA content. This was due to the autocatalytic effect, as discussed in the next section. The residual weights of the copolymers after the deprotection were slightly lower than the calculated one. The

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**Table 1. Synthesis of BHEA-Containing Polymers by Radical Polymerization in Anisole at 60 °C for 3 h**

| polymer | [BHEA]/[2EHA]/[HEA]/[AIBN] in feed (molar ratio) | polymer yield (%) | [BHEA]/[2EHA]/[HEA] in copolymer (molar ratio) | \(M_w\) \(\times 10^{-5}\) | \(M_w/M_n\) | \(T_g\) (°C) |
|---------|-----------------------------------------------|------------------|-----------------------------------------------|-----------------|----------------|-------------|
| P1      | 200/0/0/1                                      | 78.0             | 100/0/0/1                                      | 2.82            | 2.37           | 20.0 (35.5) |
| P2a     | 140/60/0/1                                     | 70.0             | 70.2/29.8/0/1                                 | 2.20            | 2.15           | −12.5       |
| P2b     | 100/100/0/1                                    | 77.3             | 50.1/49.9/0/1                                 | 1.96            | 2.86           | −29.4       |
| P2c     | 60/140/0/1                                     | 89.6             | 27.8/72.2/0/1                                 | 1.51            | 2.69           | −60.9       |
| P2d     | 40/160/0/1                                     | 87.9             | 19.2/80.8/0/1                                 | 1.60            | 2.50           | −61.4       |
| P2e     | 20/180/0/1                                     | 86.7             | 10.6/89.4/0/1                                 | 1.46            | 2.52           | −64.1       |
| P3a     | 90/90/20/1                                     | 40.8             | 38.1/46.2/13.7                                | 2.72            | 2.31           | −26.6       |
| P3b     | 70/70/60/1                                     | 63.0             | 25.7/35.0/40.3                                | 6.32            | 2.59           | −21.7       |
| P3c     | 50/50/100/1                                    | 68.0             | 17.0/28.4/54.6                                | /               | /              | −18.0       |

"Monomers/anisole = 1/4 in weight ratio. b Determined by \(^1\)H NMR spectroscopy. c Determined by size exclusion chromatography (SEC). d Determined by differential scanning calorimetry (DSC). e After deprotection. f Insoluble in tetrahydrofuran (THF)."

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**Table 2. Thermal Degradation of BHEA-Containing Polymers at the Heating Rate of 10 °C/min in Nitrogen Stream**

| polymer | \(T_d\) (°C) | \(T_{\text{max}}\) (°C) | residual weight after deprotection (%) | \(T_d\) (°C) | \(T_{\text{max}}\) (°C) | residual weight at 500 °C (%) |
|---------|---------------|-------------------------|----------------------------------------|---------------|-------------------------|-------------------------------|
| P1      | 199           | 215                     | 53.3 (53.7)                            | 259           | 419                     | 9.6                           |
| P2a     | 191           | 224                     | 65.1 (66.0)                            | 255           | 413                     | 0.6                           |
| P2b     | 195           | 229                     | 71.8 (75.0)                            | 267           | 416                     | 0.5                           |
| P2c     | 225           | 219                     | 84.6 (85.6)                            | 288           | 347                     | 3.4                           |
| P2d     | 233           | 239                     | 88.8 (89.9)                            | 280           | 340                     | 4.0                           |
| P2e     | 239           | 243                     | 91.5 (94.3)                            | 290           | 375                     | 0.4                           |
| P3a     | 194           | 226                     | 78.9 (79.6)                            | 273           | 407                     | 5.8                           |
| P3a\(^c\) | 190           | 226                     | 80.4 (79.6)                            | 316           | 421                     | 4.5                           |
| P3b     | 177           | 213                     | 82.5 (84.5)                            | 308           | 421                     | 2.0                           |
| P3c     | 170           | 208                     | 87.1 (88.8)                            | 314           | 454                     | 6.5                           |

"Values in parentheses indicate theoretical values for quantitative deprotection of BOC group. \(^c\) In the presence of hexamethylene diisocyanate (HDI) as the cross-linker (15 wt %). \(^d\) In the presence of Zn(acac)\(_2\) as the Lewis acid (3 wt %)."
BHEA-containing polymers synthesized in this study were stable at room temperature, and no change was observed after they were stored for several months. The \( T_g \) value of \( \text{P1} \) was 20.0 °C, which increased to 35.5 °C by the deprotection of the BOC group during heating at 200 °C for 30 min. The homopolymer of HEA was expected to be produced after the quantitative deprotection of the BOC group of PBHEA. The second-step degradation of the resulting polymers after the deprotection of the BOC group occurred and accompanied by a moderate weight loss in the wide temperature range of 250–450 °C, being different from the rapid weight loss for the first-step BOC deprotection. The second-step degradation included various kinds of reactions, such as ester decomposition, transesterification, ether formation, main chain scission, etc.

**Degradation Mechanism of BOC Groups.** The process of the transformation of the BOC group was investigated by IR spectroscopy. A change in the IR spectrum was monitored during heating at 200 °C using the polymer films cast on a silicon plate. A change in the IR spectrum of \( \text{P1} \) is shown in Figure 2. After heating, the polymers became insoluble in organic solvents. The intensities of a peak due to the C=O stretching vibration of the carbonate group at 1738 cm\(^{-1}\), four peaks due to the C–H stretching vibrations of the methyl and methylene groups at 2860–2959 cm\(^{-1}\), and a peak due to the O–C–C out-of-plane deformation vibration of the tert-butoxy group at 1165 cm\(^{-1}\) rapidly decreased according to the heating time within the initial several minutes. A broad absorption due to the O–H stretching vibration simultaneously appeared around 3400 cm\(^{-1}\), and its intensity increased. No change was observed after further heating. This supported the formation of the polymer of HEA by the rapid and quantitative deprotection of the BOC group in the side chain of \( \text{P1} \). Similar changes were observed for the copolymers, as shown in Figure S5. On the basis of the analysis of the peak intensity changes, we determined the conversion of the BOC group to the hydroxy group. The time–conversion curves for \( \text{P1} \) and the \( \text{P2s} \) are shown in Figure 2b. This plot indicated that the deprotection of \( \text{P1} \) occurred very fast and the transformation completely finished within 10 min. In contrast, the reaction slowly proceeded for the \( \text{P2s} \). The complete deprotection was achieved by a longer heating. The deprotection rate depended on the BHEA content in the copolymer.

It was previously reported that an autocatalytic deprotection process was observed for the BOC-containing polymers based on the analysis of the weight-loss curves of TG under the isothermal deprotection conditions at different temperatures. We also checked the reaction mechanism for the deprotection of the BOC-containing acrylate polymers. The weight loss curves at a constant temperature (200 °C) for \( \text{P1} \) and the \( \text{P2s} \) are shown in Figure 3a. These TG curves were converted to the time–conversion curves as shown in Figure 3b. The results obtained from the IR and TG analyses in the present study...
were consistent with each other. The S-shape time–conversion curves suggested the contribution of an autocatalytic reaction mechanism\textsuperscript{61} for the deprotection of the BOC group (see also Figure S4 in the Supporting Information). It was noted that the order of the $T_{ds}$ values was P2b (195 °C) > P3a (194 °C) > P3b (177 °C) > P3c (170 °C), which well agreed with the content of the HEA repeating units in the copolymer, as shown in Table 2. An increase in the $T_{ds}$ values for the P2s with a decrease in the BHEA content in the copolymers, i.e., P2a (191 °C) < P2b (195 °C) < P2c (225 °C) < P2d (233 °C) < P2e (239 °C), can be accounted for by the probability of the consecutive sequence of the BHEA units. It was speculated that an autocatalytic reaction was promoted by the interaction of an aliphatic hydroxy group produced by the deprotection, as shown in Scheme 4. The magnitude of the autocatalytic reaction of the present system was lower than that for the BOC-protected phenols, due to a high $pK_a$ value for alcohols.

**Scheme 4. Autocatalytic Deprotection of BOC Groups in Acrylate Copolymers upon Heating**

![Scheme 4](image_url)

**Shear Holding Power and 180° Peel Tests.** Figure 4 and Table 3 summarize the results of a shear holding power test using the P2s and P3b as the adhesive polymers: (Δ) P2a, (○) P2b, (□) P2c, (×) P2e, and (◇) P3b. Closed symbols indicate $T_f$ values more than 60 min.

![Figure 4](image_url)

**Figure 4.** Results for shear holding power test using the P2s and P3b as the adhesive polymers: (Δ) P2a, (○) P2b, (□) P2c, (×) P2e, and (◇) P3b. Closed symbols indicate $T_f$ values more than 60 min.

test using P2s and P3b as the adhesive polymers to determine a time to failure ($T_f$) and a creep distance after 60 min ($L_{60}$). The $T_f$ and $L_{60}$ values were determined using various weights in a range of 5–100 g for the 10 mm × 10 mm overlap joints at room temperature. As a result, the $T_f$ values for each adhesive were in the order of P3b $\gg$ P2a $> P2b > P2c > P2e$, as shown in Figure 4. It was confirmed that the holding time increased with an increase in the BHEA content, i.e., an increase in the $T_f$ value, based on the results for the P2s. In addition, the largest $T_f$ value for P3b indicated that the introduction of the HEA units effectively enhanced the holding power of the adhesive polymer without a change in the $T_f$ value, due to the intermolecular hydrogen bonding. Simultaneously, the $L_{60}$ values decreased by the increasing $T_f$ and the introduction of HEA units (Table 3).

When P2s and P3b were heated at 200 °C for 40 min, no failure of the joints occurred. The $L_{60}$ value was equal to zero, i.e., no creep was observed after heating. These results suggested that the holding power of the adhesive polymers increased by the enhancements of wettability and interactions at an interface between the stainless steel substrate and the adhesive polymer containing polar hydroxy groups. Previously, Sato et al. reported a decrease in the shear holding power of a dismantlable adhesion system using polyperoxides as the thermally degradable polymers,\textsuperscript{17} being different from the results observed in the present study using the BOC-protected acrylate copolymers. Although the polyperoxides were plasticized by the low-molecular-weight products formed during thermal treatment in the dismantling process, the BOC-containing acrylate copolymers were hardened and their $T_f$ values increased after the deprotection. The evolved gaseous products diffused out of the adhesives, and the remaining polar hydroxy groups showed no plasticizing effect.

On the basis of the shear holding power tests, it was revealed that the HEA-containing P3b exhibited the high holding power enough to be used as the pressure-sensitive adhesive material. The superiority of the copolymers containing a considerable amount of unprotected or BOC-protected hydroxy groups with an appropriate $T_f$ value as the dismantlable adhesive materials was verified.

The results for the peel strengths before and after heating are summarized in Table 4 and Figure 5. When the specimens for the 180° peel test were heated at 200 °C for 40 min, the formation of gas bubbles in the adhesive layer by the deprotection of BOC groups was observed for all of the samples containing the BOC groups in the side chain (Figure S6). Peel strength values before and after heating depended on the adhesive polymer structures. The peel strength of P2a before heating was 0.17 ± 0.14 N/25 mm, which was much lower than the peel strength for the commercial pressuresensitive adhesive tapes (typically 1–30 N/25 mm).\textsuperscript{39} A stick–slip phenomenon was observed during the peeling processes. This was due to the relatively high $T_g$ (−12.5 °C) of the adhesive. The peel strength increased to 0.93 ± 0.32 N/25 mm after heating. It was already described that the formation of hydroxy groups by deprotection increased the $T_g$ value. The formation of network structures of the adhesive polymer also increased the adhesion strength. P2d also showed a low peel strength (0.43 ± 0.02 N/25 mm) before heating and no change after heating because of a small content of BHEA units (19.2 mol %). Among the P2s, P2b with the appropriate $T_g$ value of −29.4 °C exhibited the most suitable properties of the dismantlable adhesion materials, i.e., high adhesion strength (7.91 ± 0.25 N/25 mm) before heating and the significant reduction of the strength (0.67 ± 0.13 N/25 mm) after heating. The relative adhesion strength after heating was less than 10% of the original strength. The change in the adhesion property was sufficient to be used as dismantlable adhesives.\textsuperscript{35,36} However, the failure mode was cohesive failure after heating (Table 4). For a dismantlable adhesion system, the interface failure occurring between a substrate and an adhesive layer is required. In the case of P2b, the adhesion property was reduced by the void formation due to the carbon dioxide and isobutene gases that evolved in the adhesive layer. To realize the selective interfacial failure, the cohesive force of the
adhesive polymers should be higher and the void formation in the adhesive layer should be suppressed. It was previously pointed out that the bubble formation in the adhesive layer tended to induce cohesive failure rather than interfacial failure during the dismantling process of the other pressure-sensitive adhesive system.

The presence of the HEA repeating unit in the copolymers was expected to increase the cohesive force of the adhesive polymers. We designed the copolymer compositions for the three-component adhesives on the basis of the composition and the adhesion properties of P2b. In this study, we prepared three kinds of HEA-containing copolymers, P3a–c. Because the \( T_g \) value of the homopolymer of HEA was \(-15 \, ^\circ \text{C}\), we could change the composition without an unexpected change in the \( T_g \) value by the addition of HEA units into the copolymers. P3a had a \( T_g \) of \(-26.6 \, ^\circ \text{C}\) and exhibited a high strength value before heating (12.5 ± 0.80 N/25 mm). Similarly, P3b with a \( T_g \) of \(-21.7 \, ^\circ \text{C}\) showed the highest value (15.3 ± 0.66 N/25 mm) as the initial adhesion property. A further increase in the HEA content increased the \( T_g \) value, leading to a decrease in the adhesion strength, as seen in the results for the peel strength of P3c in Figure 5. The adhesive strength of the P3s decreased with an increase in the heating time, being different form the results of the shear holding tests. The greatest difference in the adhesion strength before and after heating was observed for P3a.

**Table 4. Results of 180° Peel Test for BHEA-Containing Polymers**

| polymer | [BHEA]/[2EHA]/[HEA] (molar ratio) | heating conditions for dismantling | peel strength (N/25 mm) | relative strength | failure mode* |
|---------|----------------------------------|-----------------------------------|-------------------------|------------------|---------------|
| P2a     | 70.2/29.8/0                      | none                              | 0.17 ± 0.14             | 1                | I and C (1/1) |
| P2b     | 50.1/49.9/0                      | none                              | 0.93 ± 0.32             | 5.5              | C             |
| P2c     | 27.8/72.2/0                      | 200 °C, 40 min                    | 5.91 ± 0.25             | 1                | I             |
| P2d     | 10.6/39.4/0                      | none                              | 0.67 ± 0.13             | 0.90             | C             |
| P2e     | 17.0/83.2/0                      | none                              | 0.60 ± 0.25             | 0.50             | I             |
| P2f     | 50.1/49.9/0                      | 200 °C, 20 min                    | 2.83 ± 0.77             | 0.09             | C             |
| P3a     | 38.1/48.2/13.7                   | none                              | 12.5 ± 0.80             | 1                | I             |
| P3b     | 25.7/35.0/39.3                   | 200 °C, 40 min                    | 9.08 ± 0.80             | 0.73             | C             |
| P3c     | 17.0/28.4/54.6                   | none                              | 4.91 ± 1.71             | 1                | I             |
|         |                                  | 200 °C, 20 min                    | 3.12 ± 1.07             | 0.64             | C             |

*1: interfacial failure between a stainless steel plate and adhesive, C: cohesive failure of adhesive. 1Stick–slip behavior was observed. 1Ratio of interfacial to cohesive failures.

**Figure 5. Change in peel strength for (a) P2s and (b) P3s before (left, blue) and after heating at 200 °C for 40 min for dismantling (right, red).**
Rheological Property. We carried out dynamic viscoelasticity measurements of the adhesive polymers to discuss the effect of the elasticity of the adhesives on the adhesion strength and the dismantling performance. The storage modulus ($G'$) and loss modulus ($G''$) were determined at the angular frequencies ($\omega = 2\pi f$) of 0.06−200 rad/s at room temperature.

Figure 6a−d shows the plots of $G'$, $G''$, and $\tan\delta = G''/G'$ values as a function of the $\omega$ value for P2a and P3a before heating. As usual, a shear holding power is closely related to the viscoelastic property evaluated at a low frequency. On the other hand, the peel behavior of pressure-sensitive adhesive tapes is often discussed based on the dynamic mechanical parameters observed at an angular frequency more than 10$^2$ rad/s.

In Table 5, the $G'$ and $\tan\delta$ values determined at 0.0628 and 112 rad/s are summarized. The $G'$ values were 10.0, 1.39, and 0.108 at 0.0628 rad/s and 371, 96.3, and 51.2 kPa at 112 rad/s for P2a, P2b, and P2d, respectively. The order in these values was the same as the orders in the $T_g$ values and the shear holding power. The $G'$ values were higher than the corresponding $G''$ values, i.e., $\tan\delta$ was greater than unity over the whole frequency range for the P2s, as shown in Figure 6a−c. This indicated that the adhesive materials used in this study were typical viscous fluids. P2d partially exhibited an elastic property in the peel test (low peel strength and stick−slip behavior). This was understood by the rheological behavior of this adhesive shown in Figure 6c, in which the $G'$ and $G''$ curves integrate and $\tan\delta$ became almost unity at frequencies over 10 rad/s.

After heating at 200 °C for 40 min for the dismantling process, the $G'$ values increased and the $\tan\delta$ values became less than unity (Figure 6e) because the adhesive polymers changed from a fluid to elastic one. It was revealed that intermolecular hydrogen bonding between the HEA units produced by the thermal deprotection of the BOC groups significantly contributed to an increase in the $G'$ value at a low angular frequency (i.e., a change in the value from 1.39 to 13.0 kPa for P2b, as shown in Table 5). The HEA-containing P3a exhibited higher $G'$ and lower $\tan\delta$ values compared to P2b without HEA units before heating. The changes observed in the $G'$ and $\tan\delta$ values after heating for P3a were also noteworthy, being similar to the results for P2b. Thus, viscoelastic data supported the efficient network formation by cross-linking due to the presence of the HEA repeating units in the copolymer. The cross-linking structure was confirmed by the determination of the insoluble fractions. The insoluble fraction reached 59% after heating at 200 °C for 40 min, as shown in Table 6.

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**Table 5. Viscoelastic Parameters Determined for BHEA-Containing Polymers at Different Angular Frequencies**

| polymer | [BHEA]/[2EHA]/[HEA] in copolymer (molar ratio) | heating conditions for dismantling | at 0.0628 rad/s | at 112 rad/s |
|---------|-----------------------------------------------|----------------------------------|---------------|-------------|
|         |                                               |                                  | $G'$ (kPa)    | $\tan\delta$ |
| P2a     | 70.2/29.8/0                                   | none                            | 10.0          | 1.09        |
| P2b     | 50.1/49.9/0                                   | none                            | 1.39          | 1.93        |
| P2d     | 19.2/80.8/0                                   | none                            | 0.108         | 5.32        |
| P3a     | 38.1/48.2/13.7                                | none                            | 5.48          | 1.30        |
| P3a$^a$ | 38.1/48.2/13.7                                | none                            | 19.7          | 0.119       |
|         |                                               | 200 °C, 40 min                   | 408           | 0.606       |
|         |                                               |                                  | 200 °C, 40 min | 55.5        |

$^a$With HDI (10 wt %) and Zn(acac)$_2$ (3 wt %). $^b$Without preheating. $^c$Not determined because they were too high.

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**Rheological Property.** We carried out dynamic viscoelasticity measurements of the adhesive polymers to discuss the effect of the elasticity of the adhesives on the adhesion strength and the dismantling performance. The storage modulus ($G'$) and loss modulus ($G''$) were determined at the angular frequencies ($\omega = 2\pi f$) of 0.06−200 rad/s at room temperature. Figure 6a−d shows the plots of $G'$, $G''$, and $\tan\delta = G''/G'$ values as a function of the $\omega$ value for P2s and P3a before heating. As usual, a shear holding power is closely related to the viscoelastic property evaluated at a low frequency. On the other hand, the peel behavior of pressure-sensitive adhesive tapes is often discussed based on the dynamic mechanical parameters observed at an angular frequency more than 10$^2$ rad/s.

In Table 5, the $G'$ and $\tan\delta$ values determined at 0.0628 and 112 rad/s are summarized. The $G'$ values were 10.0, 1.39, and 0.108 at 0.0628 rad/s and 371, 96.3, and 51.2 kPa at 112 rad/s for P2a, P2b, and P2d, respectively. The order in these values was the same as the orders in the $T_g$ values and the shear holding power. The $G'$ values were higher than the corresponding $G''$ values, i.e., $\tan\delta$ was greater than unity over the whole frequency range for the P2s, as shown in Figure 6a−c. This indicated that the adhesive materials used in this study were typical viscous fluids. P2d partially exhibited an elastic property in the peel test (low peel strength and stick−slip behavior). This was understood by the rheological behavior of this adhesive shown in Figure 6c, in which the $G'$ and $G''$ curves integrate and $\tan\delta$ became almost unity at frequencies over 10 rad/s.

After heating at 200 °C for 40 min for the dismantling process, the $G'$ values increased and the $\tan\delta$ values became less than unity (Figure 6e) because the adhesive polymers changed from a fluid to elastic one. It was revealed that intermolecular hydrogen bonding between the HEA units produced by the thermal deprotection of the BOC groups significantly contributed to an increase in the $G'$ value at a low angular frequency (i.e., a change in the value from 1.39 to 13.0 kPa for P2b, as shown in Table 5). The HEA-containing P3a exhibited higher $G'$ and lower $\tan\delta$ values compared to P2b without HEA units before heating. The changes observed in the $G'$ and $\tan\delta$ values after heating for P3a were also noteworthy, being similar to the results for P2b. Thus, viscoelastic data supported the efficient network formation by cross-linking due to the presence of the HEA repeating units in the copolymer. The cross-linking structure was confirmed by the determination of the insoluble fractions. The insoluble fraction reached 59% after heating at 200 °C for 40 min, as shown in Table 6.
The dismantlable adhesion properties of the system using P3a together with HDI and Zn(acac)2 were also investigated. We checked the independent additive effect of HDI and Zn(acac)2. As shown in Table 7, the adhesion systems including 5 or 10 wt % of HDI showed a high adhesion strength (9.54–9.92 N/25 mm), similar to the adhesion strength value in the absence of HDI. After heating at 200 °C for 40 min, the adhesion strength decreased to half the original values. The addition of a higher amount of HDI resulted in the lowering of the initial adhesion strength and no change in the strength after the dismantling process under similar conditions. In Table 6, the comparison of the insoluble fractions of P3a in the absence and presence of HDI before and after heating at 200 °C for 40 min are shown. P3a was soluble in the presence of HDI before heating and it partly gave an insoluble fraction (59%) after heating. In the presence of HDI, preheating at 60 °C for 120 min resulted in the formation of a loose network structure by the reaction of the isocyanate of HDI and the hydroxy group of the HEA unit in the copolymers. Interestingly, an increase in the HDI added to the system decreased the insoluble fraction from 63 to 23% by the addition of 5–15 wt % HDI. The concentration of HDI at 5.8 wt % corresponded to the amount of the reacting hydroxy groups included in P3a. A large excess amount of HDI interrupted the cross-linking during the preheating process, leading to the formation of the polymer with isocyanate groups in the side chains, as shown in Scheme 5. The isocyanate groups incorporated in the polymer side chain further reacted with the hydroxy groups, which were produced by the deprotection of the BOC group during heating at 200 °C for 40 min for dismantling. Finally, a highly cross-linked polymer network structure was formed. The difference in the dismantlable adhesion properties in Table 7 is accounted for as follows: the preformed loose network structure interrupted the bubble formation in the adhesive layer. As a result, the produced carbon oxide and isobutene rapidly diffused to the interface of the adhesive and the substrate. This was favorable for the interfacial failure for the dismantling, but the observed failure mode was a mixture of the interfacial and cohesive ones for the adhesion system in the presence of HDI. We next examined the additive effect of Zn(acac)2 on the adhesive properties. Previously, it was reported that Zn(acac)2 effectively functioned as the Lewis acid for transesterification at interfacial and cohesive failures. 

Table 7. Results of 180° Peel Test of P3a in the Presence of HDI and Zn(acac)2

| HDI (wt %) | Zn(acac)2 (wt %) | heating conditions for dismantling | peel strength (N/25 mm) | relative strength | failure mode* |
|-----------|------------------|-----------------------------------|-------------------------|-----------------|--------------|
| 5 b       | 0                | none                              | 9.54 ± 0.06             | 1               | I            |
|           |                  | 200 °C, 40 min                    | 6.07 ± 0.74             | 0.64            | C            |
| 10 b      | 0                | none                              | 9.92 ± 1.26             | 1               | I            |
|           |                  | 200 °C, 40 min                    | 4.91 ± 1.73             | 0.49            | I and C (2/3) |
| 15 b      | 0                | none                              | 5.18 ± 1.62             | 1               | I            |
|           |                  | 200 °C, 40 min                    | 5.95 ± 1.21             | 1.15            | I and C (2/3) |
| 0         | 3                | none                              | 4.47 ± 0.39             | 1               | I            |
|           |                  | 200 °C, 5 min                     | 4.60 ± 1.57             | 1.03            | C            |
|           |                  | 200 °C, 10 min                    | 1.44 ± 1.25             | 0.32            | C            |
|           |                  | 200 °C, 20 min                    | 0.56 ± 0.17             | 0.13            | C            |
|           |                  | 200 °C, 40 min                    | 0.28 ± 0.07             | 0.06            | C            |
| 10        | 3                | none                              | 3.31 ± 0.53             | 1               | I            |
|           |                  | 200 °C, 20 min                    | 0.48 ± 0.11             | 0.15            | I            |

*1: interfacial failure between a stainless steel plate and adhesive, C: cohesive failure of adhesive. bPreheating conditions: 60 °C for 120 min. cRatio of interfacial and cohesive failures. dWithout preheating.
a high temperature in the self-repairing materials system by dynamic covalent bonding.\textsuperscript{64} We found that the addition of Zn(acac)$_2$ shortened the heating time for dismantling in our adhesion system. The adhesion strength decreased after a 10 min heating in the presence of Zn(acac)$_2$ (Table 7). The relative adhesion strengths reached 13\% during 20 min heating. The solubility test of the polymers revealed the remarkable acceleration of the cross-linking reactions by the addition of Zn(acac)$_2$. A large amount of polymers was cross-linked to provide the insoluble fraction in a high yield after heating for only 5 min (Table 6). The void formation by gas evolution was increasingly observed with an increase in the heating time, as shown in Figure S8. The larger amount of gas evolution at a shorter time was favored for an effective dismantling process.

For the adhesion system with the simultaneous use of HDI and Zn(acac)$_2$, the adhesion strength was 3.31 ± 0.53 N/25 mm before heating, and it decreased to 0.48 ± 0.11 N/25 mm after heating at 200 °C for 20 min. The initial strength value was lower than that in the absence of HDI and Zn(acac)$_2$. This was because a cross-linking reaction occurred to produce a loose network structure even after mixing the adhesive polymers with HDI and Zn(acac)$_2$ without preheating. The rheology measurement proved the formation of an elastic material before any heat treatment (Figure S9). It was also noteworthy that the interfacial failure between the substrate and the adhesive layer was completely achieved in this case. This was due to the high-density network of the adhesive polymers after heating for dismantling. It exhibited a high elasticity and cohesion force. The $G'$ value of the adhesive after heating for the dismantling (200 °C for 20 min) became too high to be determined by rheology measurements. After the sufficient progression of transesterification, i.e., the formation of cross-linking structures, the peel strength decreased due to its increased modulus. To design the adhesion system with an ideal interfacial failure, the forming of a dense network polymer structure was important before the deprotection of the BOC groups. It was already suggested that gas bubble formation was suppressed by the presence of a network structure with a short distance between the cross-linking points because the suppressed mobility of the polymer chains limited the formation of a large space needed for the growing gas bubbles.\textsuperscript{63} As a result, the evolved carbon dioxide and isobutene molecules diffused in the adhesive layer and were released at the interfaces. This supported the selective interfacial failure of the present system.

\section*{CONCLUSIONS}

In the present study, we synthesized several polymers containing the BHEA repeating unit by radical polymerization, i.e., the homopolymer of BHEA, P$_1$, the copolymers of BHEA with 2EHA, P$_2$s, and the copolymers of BHEA with 2EHA and HEA, P$_3$s. The BOC groups introduced into the side group of these polymers degraded at approximately 200 °C to provide the HEA repeating unit accompanying the evolution of carbon dioxide and isobutene as gaseous products. The degradation temperature was influenced by the composition and sequence of the BHEA unit in the copolymers because the deprotection of the BOC group was accelerated by the autocatalytic reaction mechanism. On the basis of the results for the 180° peel test of the pressure-sensitive adhesive tapes using the adhesive copolymers containing the BOC groups, P$_{2a}$ containing the BHEA units of 70 mol \% and P$_{3b}$ containing the BHEA units of 26 mol \% and the HEA units of 39 mol \% exhibited high adhesion strength required as the pressure-sensitive adhesives and the peel strength values decreased to less than 10\% of the original strength after heating to 200 °C for 20 min. The use of HDI and Zn(acac)$_2$ as the cross-linker and the Lewis acid was valid for the quick response and the achievement of the selective interfacial failure, which were required as the dismantlable adhesion materials. High-performance adhesion systems including the dismantlable adhesion materials will become a powerful tool for forthcoming materials design using various composite materials in combination with dissimilar materials bonding systems,\textsuperscript{65} which have been rapidly growing in recent years.

\section*{EXPERIMENTAL SECTION}

\subsection*{General Procedures.} The $^1$H NMR spectra were recorded using ECS-400 and ECX-400 spectrometers (JEOL Ltd.,
Tokyo, Japan) with chloroform-d at room temperature. The IR spectra were recorded by an FT/IR-4600 spectrometer (JASCO Corporation, Tokyo, Japan). The polymer solution (10 wt % in toluene) was drop-cast on a silicon plate and dried at room temperature in vacuo. The number- and weight-average molecular weights (Mn and Mw, respectively) were determined by SEC in tetrahydrofuran (flow rate at 0.8 mL/min) as the eluent at 40 °C using a system consisting of PU-2080-Plus (pump) and DG-2080-53 (degasser) (JASCO Corporation, Tokyo, Japan), CS-300C (thermostat chamber, Chromato Science, Co., Ltd., Osaka, Japan), TSKgel GMHHR-N (column, Tosoh Corporation, Ltd., Tokyo, Japan), and JASCO RI-2031-Plus (refractive index detector). The molecular weights were calibrated using standard polystyrene (Tosoh Corporation, Ltd., Tokyo, Japan). Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were performed using DTG-60 and DSC-60 (Shimadzu Corporation, Ltd., Kyoto, Japan), respectively, at a heating rate of 10 °C/min in nitrogen stream (20–50 mL/min). An isothermal TG analysis was conducted, with the temperature range of 90–130 °C. Scanning electron microscopy observations were performed using a VE-9800 (Keyence Corporation, Ltd., Osaka, Japan) at an acceleration voltage of 0.8 kV after Au vapor deposition for cross-section observation to determine the thickness of the adhesive layers. A tensile lap shear test was carried out using an Autograph AGS-X 1 kN (Shimadzu Corporation, Ltd., Kyoto, Japan) at a tensile rate of 300 mm/min. The test pieces were used for the bonding strength measurement before and after heating at 200 °C for a specific time as the dismantling process. The peel strength was determined as an average value of five measurements. The rheology measurement was carried out using a HAAKE MARS III (Thermo Fisher Scientific, Waltham, MA) at the frequency of 0.01 rad/s (i.e., ω = 0.0628–198.7 rad/s) and 25 °C with 1% strain using parallel plates.

Materials. HDI, Zn(acac)2, tert-butyl dicarbonate, and DMAP were purchased from Nacalai Tesque, Kyoto, Japan, and used as received. 2EHA (Nacalai Tesque, Kyoto, Japan) and HEA (Tokyo Chemical Industry Corporation, Ltd., Tokyo, Japan) were distilled before use. AIBN was purchased from Wako Pure Chemical Industries, Ltd., Japan, and recrystallized from chloroform. Commercially available solvents were used without further purification.

Synthesis of BHEA. To HEA (4.64 g) and tert-butyl dicarbonate (8.73 g) in 10 mL of toluene, DMAP (0.49 g) was added and stirred for 24 h at room temperature.42 To the reaction mixture, 40 mL of chloroform was added and washed with 5% aq HCl (40 mL, three times); then, the organic layer was dried over anhydrous magnesium sulfate. After filtration, the mixture (9/1 in volume) to precipitate the polymers. The polymers were isolated by decantation and purified by repeated precipitations. The polymers were dried at 60 °C under reduced pressure and used for the SEC, NMR, DSC, and TG measurements. The compositions of the copolymers were determined by 1H NMR spectroscopy.

Deprotection of BOC Groups. On the basis of the peak intensity change in the IR spectrum during heating, we determined the conversion of the BOC group to the hydroxy group according to the following equation

\[ \alpha = \frac{(A_0 - A_f)}{(A_0 - A_w)} \times 100(\%) \]

where A0, Af, and Aw are the absorbance before and after heating for a determined and after infinite times, respectively.

Shear Holding Power Test. The shear holding power test was performed according to a modified procedure of the standard test method for shear adhesion of pressure-sensitive tapes (ASTM D3654). A stainless steel plate (SUS430, 50 mm × 10 mm × 0.5 mm) was cleaned by ultrasonication in toluene for 15 min and dried in air at room temperature. Typically, two drops of a toluene solution of the adhesive polymer (10 wt %) were spread in an area of 10 mm × 10 mm and dried in vacuo for 2 h, and the mating surfaces were pressed together. The specimen was clamped and kept at room temperature for 30 min. The adhered area was fixed at 100 mm² (10 mm × 10 mm overlap joint). Various weights in the range of 4.9–100 g were used and we recorded the time to failure (Tf) and/or the creep distance after 60 min (L0) at room temperature. Typically, the average value of three measurements was adopted.

180° Peel Test. The adhesion tests were performed according to the standard test method for the peel adhesion of pressure-sensitive tape (ASTM D3330) using a universal testing machine, an Autograph AGS-X with a 1 kN (at maximum) load cell. A toluene solution of the adhesive polymers (15 wt %) was coated at a thickness of 100 μm on a poly(ethylene terephthalate) (PET) film (50 μm thickness) using a film applicator (Tester Sangyo Corporation, Ltd., Saitama, Japan) and dried overnight under reduced pressure at room temperature. The thickness of the adhesive layer was 8 μm. A strip of the PET film (25 mm width) coated with the adhesive polymers was placed on a stainless steel plate (SUS430, 50 mm × 150 mm × 0.5 mm) and then pressed using a 2 kg hand roller at the rate of 20 mm/s (twice). For the thermal treatment at 200 °C, the test piece was placed in a preheated oven for a predetermined time, removed from the oven, and then naturally cooled to room temperature. The 180° peel tests were carried out after the specimen was left to stand for 30 min at room temperature. The tensile rate was 300 mm/min. All of the adhesion tests were performed at 25 °C. The average value of five measurements was recorded. For the adhesive materials containing HDI, the mixture of the adhesive polymer and HDI in toluene was heated at 60 °C for 120 min in the presence or absence of (Zn(acac)2).

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02371.
NMR spectra, TG curves, analysis of degradation rates, IR spectra, photographs of specimens for 180° peel test, and rheology measurement data (PDF).

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**Notes**
The authors declare no competing financial interest.

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