REVIEW

Development of heat-responsive adhesive materials that are stable during use and quickly deteriorate during dismantling

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Abstract

When developing functional adhesives, material design is generally based on incorporating additional function without sacrificing the original adhesive performance. In contrast, the development of dismantlable adhesive materials—adhesives with on-demand debonding function—requires a different approach from ordinary functional adhesive materials since the function of disassembly is opposite to that of adhesion. In this review article, the author first provides an overview of recent studies on heat-responsive and photoresponsive adhesive materials and the characteristics of other external stimuli used for dismantlable adhesive systems. Then, research on dismantlable adhesive materials using polyperoxides is introduced as an example of early material design. Research trends in the synthesis of degradable polymers by radical polymerization, which are closely related to future environmental issues, are briefly referenced. Next, the development processes of dual-stimuli responsive dismantlable adhesive materials are interpreted as a guideline for the material design to achieve stability during use and degradability during dismantling. Finally, recent studies on heat-responsive dismantlable adhesive systems, in which thermal stability during use is prioritized while responding quickly during disassembly by heating, are described.

Introduction

Functions often needed for adhesives include high strength, high reliability, weather resistance, shock absorption, high- and low-temperature properties, high electrical conductivity, excellent electrical insulation, high thermal conductivity, heat-shielding properties, ease of disassembly, dissimilar material bonding, degradability, low environmental impact, and sustainability [1–5]. To develop functional adhesives, the material design incorporates additional functions without sacrificing the original adhesive performance as much as possible. However, since the function of disassembly is opposite to that of adhesion, the development of dismantlable adhesive materials—adhesives with on-demand debonding function—requires a completely different approach from other functional adhesive materials [6–8].

Among the adhesive materials that have been developed thus far, adhesive materials that are clearly designed to exhibit an easy-to-dismantle function are used in relatively special fields and applications. For example, dicing tape is used to temporarily fix components in the semiconductor manufacturing process [9]. The superior technology and materials used in semiconductor manufacturing tapes might be readily applicable to other fields, but there are actually few examples of these technologies being used in easily dismantled adhesive materials for general use. The minimal application arises because the usage environment and disassembling conditions for semiconductor manufacturing tapes are significantly different from those for general adhesives, including pressure-sensitive adhesives (PSAs). In contrast to the ability to strictly control the environments and conditions in which semiconductor manufacturing tapes are handled during the entire manufacturing process, easily removable adhesives intended for general purposes are used in multiple applications and multiple products under loose management conditions. In regard to previously developed dismantlable adhesive materials, materials and methods are often developed individually depending on the application and requirements, and it is difficult to use a single material or method for widespread use.

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In this review article, we first provide an overview of recent studies on heat-responsive and photoresponsive adhesive materials and the characteristics of other external stimuli used for dismantlable adhesive systems. Then, we introduce our research on dismantlable adhesive materials using polyperoxide as an example of a relatively early material designed with an emphasis on degradability. The synthesis of polyperoxides has the potential to be a useful tool for designing polymer materials with low environmental impact in terms of the synthesis of degradable polymers by radical polymerization. Therefore, we briefly discuss research trends in the synthesis of degradable polymers by radical polymerization, which are closely related to future environmental issues. Next, we mention the development of a dual-stimuli responsive dismantlable adhesive material, which is an important guideline of material design for achieving stability during use and degradability during dismantling. Finally, we explain recent studies on heat-responsive dismantlable adhesive materials that emphasize thermal stability during use while responding quickly during disassembly by heating.

Stimulus-responsive adhesives

A number of materials that exhibit a decrease in adhesion strength in response to external stimuli have been developed. Hot melt adhesives are typical simple heat-responsive adhesive systems that not only use thermally softening properties to bond but can also be disassembled if necessary. In adhesive systems, in addition to peeling or disassembly, heat and light are used as stimuli during a curing process. To improve adhesive workability using heat-curing or photocuring adhesives, there are methods for intentionally delaying the improvement in adhesion strength by adding a curing delayer and methods for postcuring at actual work sites by using heat and light. Adhesive materials have been developed with the necessary functions for each purpose, but recently, there has been increasing interest in the development of heat-responsive and light-responsive adhesives with peeling and disassembly functions.

In the synthetic design of crosslinked polymers, research is actively being conducted on methods for increasing the toughness of crosslinked polymer materials using dynamic covalent chemistry [10]. Covalent recombination reactions are classified into bond-dissociation and bond-exchange reactions. The crosslinked polymers in which bond recombination occurs through the latter reaction mechanism are called vitrimers [11, 12]. Among the research fields related to network polymer materials, vitrimers have been one of the most active research topics in the world over the past 10 years [13, 14]. Since the reactions of vitrimers do not involve the temporary dissociation of crosslinking points during bond exchange, the number of crosslinking points is maintained at a constant level simply by increasing the exchange rate at high temperatures. As a result, the vitrimers exhibit a small change in fluidity with increasing temperature. This point is significantly different from ordinary polymer materials, in which the viscosity rapidly decreases and becomes liquefied when heated above a glass transition temperature (T_g) or softening point. Vitrimer materials are suitable for reworkability and repairability since they have a relatively low fluidity at a high temperature and can maintain a certain shape without using a mold.

Unlike adhesives originally intended to be removed and used for temporary fixation, high adhesion strength must be maintained throughout. The adhesion strength generated during the curing process must not deteriorate over time and must last for a long period. Adhesives that require high strength and toughness often include a crosslinked network polymer structure during the bonding process. The better the adhesive performance with the strong crosslinked structure, the more difficult the peeling and disassembly processes. Furthermore, compared with thermoplastic polymers, crosslinked polymers are less susceptible to creep, and it is often difficult to eliminate stress concentration and to avoid the formation of defective structures.

Incorporating a bond-exchangeable structure into a crosslinked polymer can impart reversibility to adhesive properties, making it possible to apply it to removable adhesive materials and self-healing materials [15–17]. For example, reversible adhesives that utilize dynamic covalent bond exchange reactions have been developed. The effects of bond exchange reactions on the adhesive properties and the repeated use properties of disulfide group-introduced epoxy adhesives have been investigated [18]. The breaking strength in a shear tensile test before heating is equivalent to that of an epoxy adhesive that does not contain disulfides. Furthermore, when the test pieces are brought into contact again and heated after being disassembled and peeled, the adhesion strength recovers to approximately 90% if at least one of the epoxy resins and the amine curing agent contain a disulfide group. When neither the resin nor the curing agent contains disulfide, almost no strength is recovered. Similar material design is possible with materials other than disulfide bonds, and good repair effects have been observed with cured epoxy products containing functional groups that effectively act on transesterification [19, 20]. Bonding using epoxy adhesives inevitably causes stress concentration due to thermal contraction caused by heating and cooling, but the effect of mitigating these thermal stresses has been confirmed.

Photoresponsive materials include many characteristics that differ from those of heat-responsive materials [21–23].
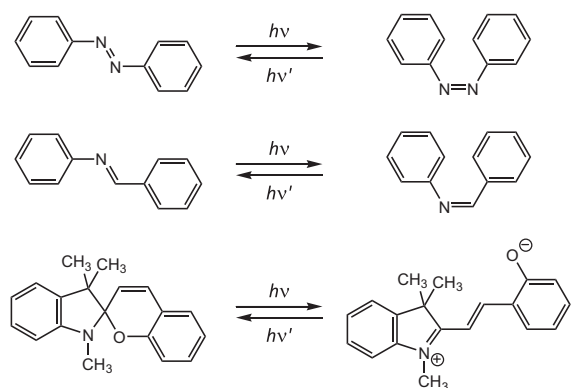
Fig. 1 Examples of probe molecules for photoisomerization reactions, which are used as a trigger inducing the phase transition of entire adhesive materials by a small change in their molecular structural changes. A thermal stimulus is sometimes used for reverse reactions

Using light as an external stimulus for reversible adhesive design has the following advantages: high spatial and temporal resolution, noncontact irradiation possible, use of adherends and media with high thermal conductivity, use of liquids including water as reaction media, and uniform irradiation over large areas. Conversely, it is possible to apply optical stimulation to a very local, narrow, specific range. Furthermore, irradiation conditions, such as intensity, wavelength, on/off cycle, and polarization, can be finely adjusted, unlike thermal stimulation, where the factors for reaction control are almost limited to temperature and time.

To significantly change the adhesion force through external stimulation through light irradiation, it is necessary to use the photoreaction as a trigger to change the molecular structure and physical properties of the entire material. For example, reversible systems involving the phase transition of the entire adhesive material caused by molecular structural changes due to photoisomerization have been reported [7]. Several systems have been proposed by using azobenzene [24–27], benzylideneaniline [28], spiropyran [29, 30], etc., as probe molecules for photoisomerization reactions to elicit discontinuous changes in physical properties that occur with isomerization (Fig. 1). In addition to isomerization, there have been reports of the formation of polymer networks by [2 + 2] photodimerization and [4 + 4] photocycloaddition and the use of reverse cleavage reactions (decrosslinking) by irradiation or heating [31, 32]. Ultraviolet (UV) or visible light is advantageous in terms of equipment and cost relative to short-wavelength electromagnetic wave irradiation, such as X-rays and electron beams. In addition, by using near-IR light, which has excellent penetration and invasiveness, photoresponsive adhesive systems are expanding into biological systems [33].

When a reaction is induced by light irradiation, it is inevitable that there will be differences in light absorption in the depth direction, with the exception of thin-film samples, and this phenomenon often results in the difficulty for the reaction to proceed father into the material. This result occurs because the reaction requires absorption of light of a specific wavelength, but the intensity of transmitted light attenuates exponentially in the depth direction. To accelerate the reaction even in the internal regions of the material, some methods, such as the combination of photocuring and heat curing [34] and frontal polymerization, are used [35, 36].

External stimuli for dismantling

Adhesive bonding is an essential technology for joining dissimilar materials and is used to assemble products with complex structures that combine different materials, such as metals, inorganic materials, and organic materials [37]. Products that have reached the end of their useful life are dismantled, collected according to their material types, and reused as resources. Nevertheless, using an adhesive that is stronger than necessary will impede product disassembly. The development of new adhesive materials and adhesive technologies is progressing daily to create an adhesive system that maintains high-adhesive properties when the product is during use but can be easily peeled off and dismantled by applying an external stimulus after use. It is important to note that the product lifespan and necessary strength vary widely depending on the application and field. Warranty periods for adhesives used in products are different at an age of a few days (for example, in biorelated applications) and at an age of over 100 years (for example, in architectural applications). It is important to appropriately select adhesive materials and systems according to each purpose and requirement. Improving recyclability is an essential requirement in several fields, such as home appliances, automobiles, IT, and OA; increasing the efficiency of separating resins, glasses, and metals and recovering rare metals have become urgent issues.

However, as mentioned at the beginning, it is not always easy to simultaneously satisfy adhesion and disassembly, which are contradictory properties. Dismantlable adhesion technology requires sufficient strength and stability during use, but when dismantled, it must be able to respond quickly to external stimuli and significantly reduce bond strength [8, 38–42]. It has already been mentioned that it is difficult to transfer the technology cultivated in the development of semiconductor manufacturing tapes directly to general public purposes, but there are still many things to learn from that technology. Adhesive tapes with special functions, such as back grind tape and dicing tape, are used to temporarily fix IC chips on silicon wafers in each stage of industrial semiconductor manufacturing [9, 43–46]. These

tapes are required to have both adhesion force to prevent wafers and chips from peeling off or scattering and excellent dismantling ability to be easily peeled off at the end of each work process. There are three types of dicing tape: weak adhesive type, UV-curing type, and heat-foaming type. Weak adhesive tapes are used for dicing and pickup without changing the adhesion strength in each process, but it is difficult to demonstrate high-performance adhesive and peeling functions. UV-curable and heat-foamable tapes have specifically been developed as high-performance, easily peelable tapes. UV-curable adhesive tapes undergo a curing reaction due to photocrosslinking, resulting in a decrease in strength. They utilize the unique relationship between the elastic modulus and strength of the adhesive and for PSA. The photocuring reaction of the adhesive increases its elastic modulus, and as a result of the decreases in tack and elongation, the adhesion strength rapidly decreases, resulting in self-peeling properties. The latter thermal release tape uses an adhesive material that undergoes any reaction that generates gas when heated, foams at the adhesive interface, and peels off spontaneously. The timing and position of foaming induced by the chemical reaction, particularly controlling foaming near the interface, is the key to achieving easy peeling ability.

To design an adhesive system that can be effectively dismantled, it is necessary to apply an external stimulus during disassembly to rapidly change the state of the adhesive itself or the state of the interface between the adhesive and the adherend. Candidates for external stimuli during disassembly include heat, light, ultrasonic waves, chemical reactions, and electricity, but some of these stimuli are used during the bonding process. It is important to design a system that combines different conditions for the processes of bonding and dismantling.

The dismantling processes that use light as an external stimulus utilize various photoreactions, such as photolysis, photodimerization, and photoisomerization. As already explained, the process using light irradiation has the advantage of being able to disassemble in a short time. When disassembling by photolysis, it is effective to drastically control physical properties by decrosslinking reactions that occur at specific crosslinking points. By incorporating reversible crosslinking and decrosslinking reactions into adhesive polymers, recyclability, reworkability, and self-healing properties can be imparted to the material. Various reversible reactions, such as photodimerization of coumarin and anthracene, thermal Diels–Alder reaction between furan and maleimide, dimerization due to the formation of strong hydrogen bonds, and exchange-type reactions, such as the reaction between thiols and disulfides, are used to design removable adhesives (Fig. 2) [7, 10, 47–51]. In addition to light and heat, chemical decomposition is used to decrosslinked
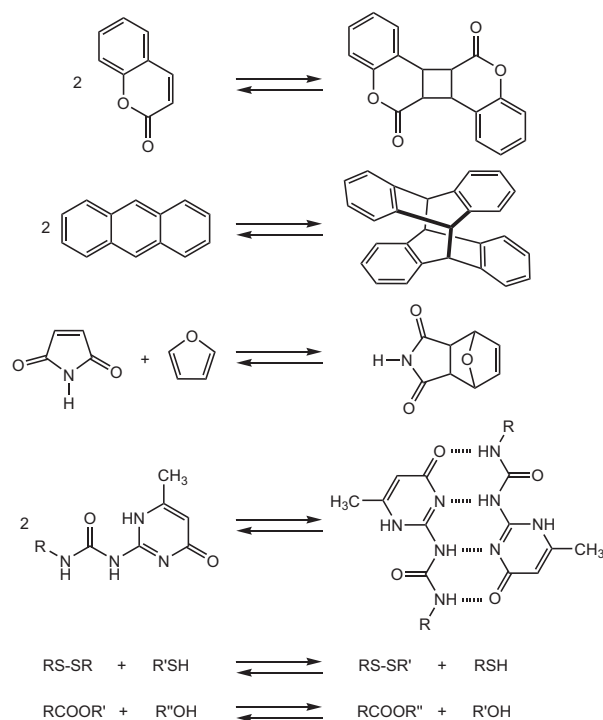

Fig. 2 Reversible crosslinking and decrosslinking reactions for the molecular design of removable adhesive materials. The reactions are classified into dimerization or heterodimerization types and exchange types

network polymers. Incorporation of diacyl hydrazine into the crosslinking sites results in a degradable polymer gel. This incorporation does not oxidize in air but rapidly decomposes under the action of sodium hypochlorite [52, 53].

Removable and dismantlable adhesion technologies that have already been put into practical use include thermoplastic adhesives, thermally expandable microcapsule adhesives, moisture-absorbing release adhesives, electromagnetic induction heating (IH), electrical release adhesives, and UV-curing adhesive tapes [6]. These systems employ methods that use physical stimuli, such as heat, light, and electromagnetic waves, as triggers to change the adhesion strength at once. As seen in microwave induction heating [54], ultrasonic welding [55], and electrically [56] peelable adhesives, the use of stimuli for disassembly, such as microwaves and electric current, that are unlikely to be applied under normal usage conditions is advantageous in terms of performance stability during use. Thus, appropriate selection of external stimuli is important for the development of high-performance dismantlable adhesive materials and technologies.

Another important factor indispensable for high-performance dismantlable adhesive materials is the concept of incorporation of a structure into the polymer that decomposes or reacts in response to external stimuli.

Fig. 3 a Changes in the molecular structures of the polymers including reactive and degradable moieties in the main chain and the side chain by any reaction in response to external stimuli. **b** Degradation reactions of the main chain and the side chain incorporated into block copolymers and graft polymers and advantages for using block copolymers

(a) Polymer reactions (degradation)

Main-chain scission

MW change   depropagation

Cross-linking and decross-linking

linear polymer   network polymer

Side-chain reaction

polymer transformation

(b) Reactions for block copolymers

block copolymer   homopolymer

branched polymer   polymer blend

block copolymer   block copolymer

Advantage for block copolymers
· Precise control of polymer properties
· Microphase separation
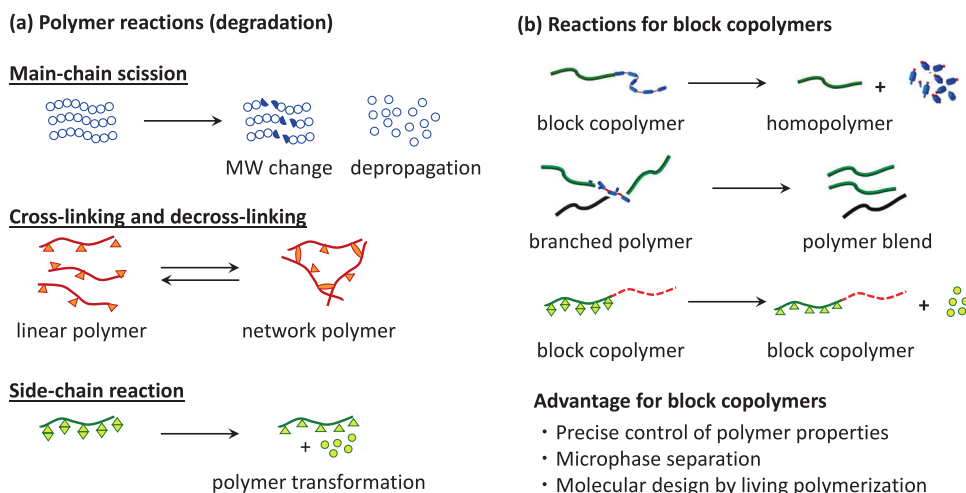· Molecular design by living polymerization

Figure 3 summarizes a schematic diagram of structural changes in polymers due to decomposition and polymer reactions. In addition to main-chain degradation, we can use decomposition and any other polymer reactions (including functional group transformation) of a functional group in the side chain. Site-specified reactions limited to selected crosslinking points and segments are valid. These reactions make it possible to bring significant changes in the physical properties of polymer materials. The author has continued to conduct research on the synthesis of new dismantlable adhesive materials, including the precise design of polymer structures. Starting with a trial for the application of thermally degradable polymers to adhesive materials, we have already developed a system that combines the reaction of polymer side chains with light irradiation and heating. Then, we succeed in constructing a new system that has excellent thermal resistance but can disassemble when stimulated by heat. Some examples of the development of dismantlable adhesive materials are introduced in the following sections.

Synthesis of degradable polymers by radical copolymerization

By utilizing radical copolymerization of nonvinyl monomers, it is possible to introduce the repeating unit into the main chain of polymers, even if the monomer is not homopolymerizable. The repeating structure produced by the copolymerization of a nonvinyl monomer is different from the sequence structure consisting of carbon-to-carbon bonds produced from a conventional vinyl monomer. Depending on the structure of the nonvinyl monomer, readily degradable bonds can be introduced into the polymer chain.

Oxygen acts as an inhibitor of radical polymerization, but it is known that oxygen can function as a monomer depending on specific conditions, such as the type of vinyl monomer used, the oxygen concentration, and the temperature [57]. For example, electron-donating vinyl monomers, such as styrene, undergo radical alternating copolymerization with oxygen to produce polyperoxides containing repeating peroxide units (–O–O–) in the main chain. Polyperoxides have a long history, with the first synthesis dating back to 1922 [58–60]. Staudinger reported that air oxidation of 1,1-diphenylethylene produces a polymeric substance that decomposes explosively when heated, with the decomposition products being benzophenone and formaldehyde. Subsequently, Mayo et al. [61], Kishore et al. [62], and De et al. [63, 64] analyzed the synthetic conditions, decomposition behaviors, and chain degradation mechanisms of polyperoxides from kinetic and thermodynamic points of view in detail. As described in their reviews, applied research utilizing the decomposition of polyperoxides has been developed in various fields.

Alternating copolymers are formed not only from vinyl monomers but also from the radical copolymerization of diene monomers with oxygen. The conventional synthesis of polyperoxide starting from vinyl monomers includes copolymerization by supplying oxygen under high-pressure conditions; however, polyperoxide can be easily obtained in a high yield by the radical copolymerization of alkyl sorbates and oxygen under atmospheric pressure conditions, as shown in Fig. 4 [65]. Subsequently, intensive research began on the synthesis of new degradable polymers using diene monomers. The potential applications of polyperoxides in several fields, including dismantlable adhesive systems, have been investigated [66–73].

The basic characteristics of the thermal properties of the polyperoxides obtained from diene monomers are explained below. The copolymerization of diene monomers with oxygen in the presence of a low-temperature radical initiator produces polyperoxides with molecular weights on the order of several thousand [74]. Table 1 summarizes the
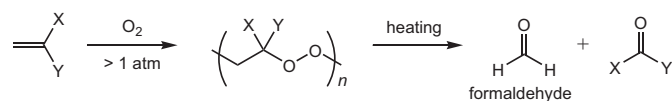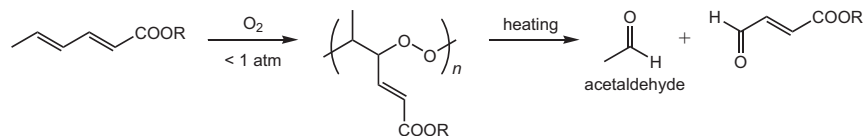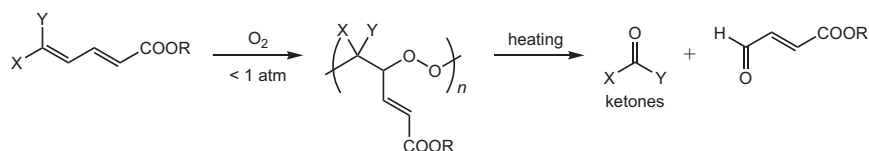
(a) Polyperoxides produced from vinyl monomers under high pressure conditions

(b) Polyperoxides produced from diene monomers under low pressure conditions

(c) Polyperoxides including no aldehyde in the degradation products by molecular design

Fig. 4 Synthesis of polyperoxides by radical alternating copolymerization of vinyl and diene monomers with molecular oxygen. **a** Polyperoxides synthesized from vinyl monomers with oxygen under high-pressure conditions. Formaldehyde is produced during the degradation of this type of polyperoxide. **b** Polyperoxides synthesized from sorbic esters with oxygen under low-pressure conditions. One of the degradation products is acetaldehyde, not formaldehyde. **c** Polyperoxides synthesized from designer diene monomers to change the chemical structures of the degradation products. It is possible to arrange the degradation products as aldehyde-free and nonvolatile compounds by the molecular design of the starting diene monomers

molecular weights, decomposition temperatures, and decomposition calorific values of the polyperoxides obtained from various diene monomers and oxygen that have been reported thus far [75–79]. The chemical structures of the monomers used as starting materials are shown in Fig. 5.

When these polyperoxides are heated, a decomposition reaction proceeds exothermically and rapidly above a certain temperature. The decomposition proceeds by a radical chain reaction mechanism and exhibits depolymerization-type reaction behavior that yields low molecular weight compounds as decomposition products. However, unlike general depolymerization, instead of returning to the starting monomer and oxygen, the oxygen radicals generated by main chain scission become carbon radicals through β-elimination, and the carbon radicals are converted into oxygen radicals by subsequent β-elimination. Most of the decomposed products immediately leave the system as volatile components. The resulting radicals undergo the same reaction repeatedly, and in the end, only two types of low-molecular-weight compounds are produced from each polyperoxide, as shown in Fig. 6 [66]. No oligomers or other products are produced during decomposition. When the number of alkyl substituents contained in the diene monomer used as a raw material is increased, the decomposition initiation temperature of polyperoxide decreases by several tens of degrees due to steric and electronic effects. In addition, the chemical structures of the decomposition

products change. When conventional polyperoxides synthesized from vinyl monomers are thermally decomposed, formaldehyde is always produced, but by using sorbic acid derivatives as raw materials, the thermal decomposition products can be replaced with low-toxicity acetaldehyde. Furthermore, by appropriately selecting the molecular structure of the diene monomer, polyperoxides that do not produce any aldehyde as a final decomposition product have been synthesized (Fig. 4) [76, 77].
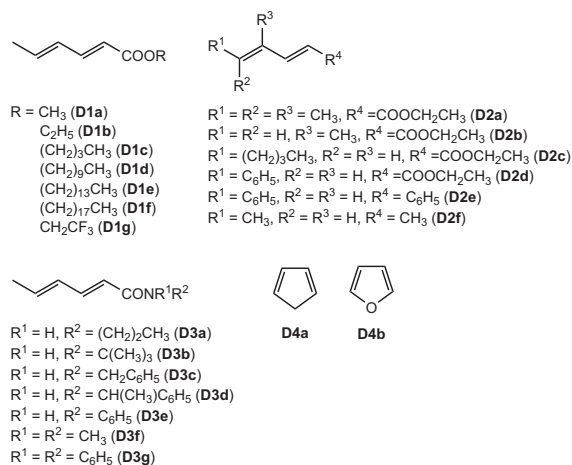
The thermal decomposition behavior of the polyperoxides, including unique depolymerization-type reactions, is closely related to the alternating propagation of diene monomers and oxygen with high regioselectivity, i.e., highly selective 5,4-propagation in the case of sorbic esters. Examples of regioselective addition reactions and polymerizations are rare via a radical reaction mechanism. To clarify the reaction mechanism exhibiting high selectivity in the alternating copolymerization of sorbic ester monomers and oxygen, the regiospecific reactions have been analyzed by computational chemistry using density functional theory (DFT) [77, 78]. The outline of the reaction mechanism is explained below.

The production of polyperoxides proceeds through a two-step regiospecific reaction during the propagation of the alternating copolymerization of sorbic acid derivatives and oxygen. These reactions include (i) regiospecific propagation in the addition of the peroxy radical to a diene monomer and (ii) regiospecific propagation in the addition of the

Table 1 Thermal degradation characteristics of polyperoxides produced from various diene monomers[a] (Fig. 5 for the chemical structure of the used monomers)

Monomer	M_n x 10^{-3}	T_{init} (°C)	T_{max} (°C)	ΔH (kJ/mol)	Ref.
D1a	3.2	108	148	187	75
D1b	4.0	107	147	-	75
D1c	4.2	106	143	148	78
D1d	7.4	105	148	179	78
D1e	7.5	106	146	163	78
D1f	8.6	112	152	191	75
D1g	5.4	107	148	-	75
D2a	5.6	69	100	164	77
D2b	4.4	82	129	167	76
D2c	3.1	89	141	166	76
D2d	2.3	72	121	163	76
D2e	2.9	76	110	176	76
D2f	5.0	95	152	262	75
D3a	0.9	88	138	145	78
D3b	1.6	87	141	189	78
D3c	1.9	101	140	189	78
D3d	1.7	107	140	182	78
D3e	2.3	108	140	212	78
D3f	0.8	86	121	252	78
D3g	2.5	102	137	212	78
D4a	2.9	129	169	-	79
D4b	1.0	88	133	-	79

[a]Polyperoxides were synthesized by radical copolymerization of diene monomers with molecular oxygen in 1,2-dichloroethane in the presence of an azo initiator at 30 °C

R = CH₃ (**D1a**)
   C₂H₅ (**D1b**)
   (CH₂)₃CH₃ (**D1c**)
   (CH₂)₉CH₃ (**D1d**)
   (CH₂)₁₃CH₃ (**D1e**)
   (CH₂)₁₇CH₃ (**D1f**)
   CH₂CF₃ (**D1g**)

$R^1 = R^2 = R^3 = CH_3$, $R^4 = COOCH_2CH_3$ (**D2a**)
$R^1 = R^2 = H$, $R^3 = CH_3$, $R^4 = COOCH_2CH_3$ (**D2b**)
$R^1 = (CH_2)_3CH_3$, $R^2 = R^3 = H$, $R^4 = COOCH_2CH_3$ (**D2c**)
$R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = COOCH_2CH_3$ (**D2d**)
$R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = C_6H_5$ (**D2e**)
$R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = CH_3$ (**D2f**)

$R^1 = H$, $R^2 = (CH_2)_2CH_3$ (**D3a**)
$R^1 = H$, $R^2 = C(CH_3)_3$ (**D3b**)
$R^1 = H$, $R^2 = CH_2C_6H_5$ (**D3c**)
$R^1 = H$, $R^2 = CH(CH_3)C_6H_5$ (**D3d**)
$R^1 = H$, $R^2 = C_6H_5$ (**D3e**)
$R^1 = R^2 = CH_3$ (**D3f**)
$R^1 = R^2 = C_6H_5$ (**D3g**)

D4a   **D4b**

Fig. 5 Chemical structures of the diene monomers used as starting materials for the synthesis of polyperoxides reported thus far (refs. [75–79]). See Tables 1 and 2

allyl radical to oxygen. A change in the enthalpy of the addition of a methyl peroxy radical to diene monomers as the model reaction (Fig. 7) is estimated, and the results are summarized in Table 2 [77, 78]. The reactions between various diene monomers and a methyl peroxy radical are all exothermic reactions. It has been revealed that the enthalpy change in the addition at the C5 position is larger than that of the addition at C2 ($\Delta H_B - \Delta H_A$ = ca. 40 kJ/mol). This difference indicates the stability of the allyl radical generated by addition to the C5 carbon, and the main factor is stabilization due to resonance with the carbonyl group. When the diene has an ester group and a phenyl group at both ends, the addition to both C2 and C5 carbons occurs competitively (**D2f** in Table 2). The role of the carbonyl group adjacent to only one side of the diene structure is important for sorbate esters, and the effect of conjugation with the carbonyl group contributes to regioselectivity.

The selectivity of the second-step reaction has been investigated in a similar manner. In general, peroxy radicals have lower reactivity than other oxy radicals and carbon radicals; therefore, the reaction between the carbon-centered radicals and oxygen is reversible. Porter et al. calculated bond dissociation energies (BDE) for the C–OO• bond of peroxy radicals with various substituents [80] and found that the C–OO• bond is stabilized for peroxy radicals with electron-donating substituents, including conjugated groups, by hyperconjugation between the group and the σ_{C-O*} orbital of C–OO• and destabilized by an inductive effect when electron-withdrawing substituents are introduced [81]. It has been confirmed that the BDE of the peroxyl radicals is correlated with the rate constant of β-cleavage (k_β) and that the larger the BDE is, the smaller k_β.

Table 2 shows the calculation results of the BDE in the reaction between the allyl radicals and oxygen. Herein, we assume that the methyl peroxy radical is added to the C5 carbon of the sorbates and show the calculation results for the generated allyl radicals in which the C4 and C2 carbons react with oxygen ($BDE_{5,4}$ and $BDE_{5,2}$, respectively). $BDE_{5,4}$ is 57–63 kJ/mol, and $BDE_{5,2}$ is 31–40 kJ/mol for the sorbic esters (i.e., **D1a** and **D2a**). The value of $BDE_{5,4}$ is clearly large. When applying the calculation results for methyl sorbate to the relational expression between BDE and k_β, $\log k_\beta(5,4) = 2.8$ and $\log k_\beta(5,2) = 5.5$, resulting in a difference of nearly 10^3 in the depropagation rates between them. The smaller $BDE_{5,2}$ value is explained by the destabilization of the C − OO• bond due to the inducing effect of the carbonyl group substituted on the carbon of the C − OO• bond.

When similar calculations are performed for 2,4-hexadiene (**D2f**), which is a hydrocarbon diene monomer that does not have a conjugated group, the $BDE_{5,4}$ and $BDE_{5,2}$ values are approximately the same (85–86 kJ/mol). This finding shows that both 2,3- and 2,5-propagations can occur competitively, and in the copolymerization of **D2f** and oxygen, both 2,3- and 2,5-structures are generated [75]. This result agrees well with the fact that a similar tendency is observed for cyclic diene monomers, such as

Fig. 6 Thermal degradation mechanisms of polyperoxides synthesized from diene monomers. The polyperoxides have a selective 5,4-repeating structure. The degradation proceeds via a radical chain reaction mechanism to yield two kinds of degradation products as low-molecular-weight compounds
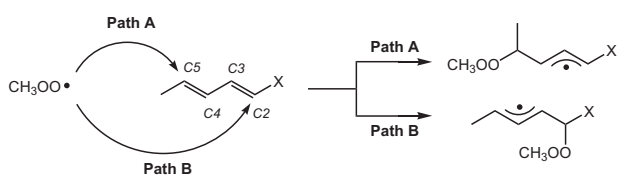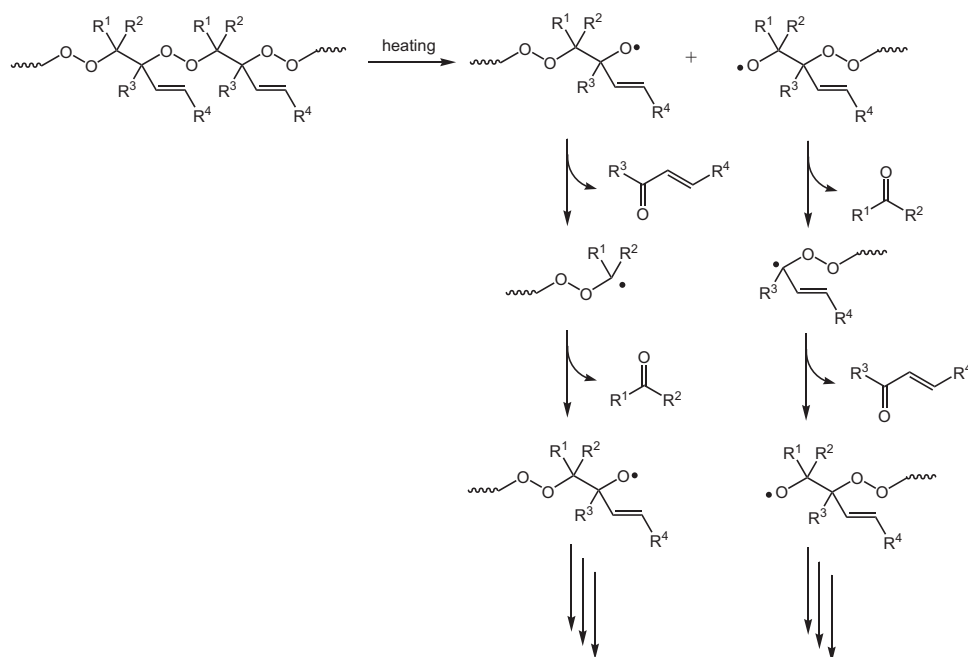

Fig. 7 Regioselectivity of the addition of a methyl peroxy radical to a diene monomer. There are possible attacks on the C5 carbon (Path A) and the C2 carbon (Path B)

cyclopentadiene (**D4a**) and furan (**D4b**), and in the propagation reaction of these cyclic monomers, the structures corresponding to the 5,2-structure in sorbic esters become somewhat predominant [79].

The conjugation property of sorbic amide varies depending on the number and structure of the *N*-substituents. Since the electron-withdrawing property of the substituent in the *N*-monosubstituted sorbic amide is lower than that of sorbic ester, selectivity in the addition of the allyl radical to oxygen is reduced. The regioselectivity (selectivity of Path A and Path B) during the addition of the oxygen radical to the dienes decreases [78]. Conversely, the carbonyl group of *N,N*-disubstituted sorbic amides (**D3f** and **D3g**) cannot form a conjugated structure with the diene moiety due to the steric hindrance of the bulky substituent, and the regioselectivity of the propagation is completely different from that of *N*-monosubstituted sorbic amide (**D3a**), as shown in Table 2. In this manner, the conjugation and electronic properties of the radicals and monomers sensitively affect the selectivity of the reaction path during propagations of the diene monomers and oxygen.

These thermally decomposable polyperoxides are used as heat-responsive and dismantlable adhesives [82, 83]. Polyperoxide that is synthesized by the radical copolymerization of methyl sorbate and oxygen, i.e., PPMS, has a T_g of $-13\,°C$, which is higher than the temperature for use as a PSA (typically $-30\,°C$). When performing a $180°$ peel test using PPMS as an adhesive, a stick–slip phenomenon is observed (Fig. 8). At this time, if PPMS is heated at $70\,°C$ for 10 min, the retention time is shortened to approximately 1/4 of that before heating. Similarly, the $180°$ peel strength decreases by a factor of approximately 10. Under these conditions, the polyperoxide decomposition rate is less than a few percent, indicating that a small amount of low-molecular-weight decomposition products function as plasticizers.

Furthermore, to rationally control the adhesive properties of the PSA polymer, a block copolymer containing a polyperoxide block sequence has been used. Based on the results of examining the applicability of various living radical polymerization (i.e., reversible-deactivation radical polymerization (RDRP)) methods, nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer polymerization (RAFT polymerization) are first selected as methods for synthesizing block copolymers. It is eventually found that when using these methods, specific problems, such as high polymerization temperature, basic ligand, and oxidation of RAFT, occur and block copolymers are not produced [83]. Conversely, reversible transfer catalytic polymerization (RTCP) is effective in the synthesis of polyperoxides [83]. It is clear that the RTCP method is

Table 2 DFT calculation results for an enthalpy change during the reactions through path A and path B and BDE of the C – OO· bond of the peroxy radicals

Monomer	ΔH_A (kJ/mol)	ΔH_B (kJ/mol)	ΔH_B–ΔH_A (kJ/mol)	$BDE_{5,4}$ (kJ/mol)	$BDE_{5,2}$ (kJ/mol)	Ref.
D1a	−41.63	−3.64	38.00	63.47	39.53	77
D2a	−49.87	−3.14	46.73	57.28	31.17	77
D2f	-	-	-	85.81	85.23	77
D3a	−41.63	−27.70	13.93	59.62	54.02	78
D3f	−42.84	−14.89	27.95	65.81	50.25	78
D3g	−40.09	−2.97	37.12	65.56	42.17	78
D4a	-	-	-	67.36–72.38[a]	74.48–74.89[a]	79
D4b	-	-	-	45.61–59.83[a]	66.11–69.04[a]	79

[a]Values calculated for cis and trans isomers

(See Fig. 7 for reaction paths)

(a) Degradation of polyperoxides

polyperoxide   degradation products

(b) Before heating

Stick-slip
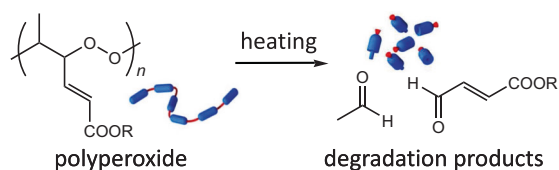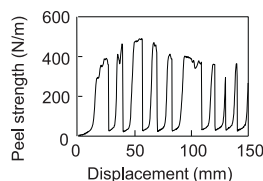
(c) After heating for 1 h

Easy pealing
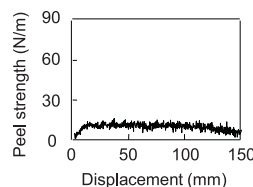
Fig. 8 a Thermal degradation of the polyperoxide synthesized from diene monomers. For PPMS, the ester alkyl group R is methyl. **b** Result of a 180° peeling test for PPMS at room temperature before heating. The T_g of PPMS is −13 °C, which is higher than the ideal T_g value for PSA. As a result, a stick–slip phenomenon is observed. **c** Result of a 180° peeling test for PPMS at room temperature after heating at 70 °C for 1 h. The peel strength is drastically reduced, and the adhesive tape is easily released from the a stainless-steel (SUS) plate as the adherend. The peeling test is carried out at room temperature

valid for the controlled polymerization of styrene and methacrylic esters [84–86], but it was unclear whether it can be adapted for other monomers at that time. Therefore, we have copolymerized methyl sorbate and oxygen using poly(2-ethylhexyl methacrylate) (P2EHMA) containing iodine at the polymer chain end as the macroinitiator, resulting in the formation of block copolymers containing polyperoxide and polymethacrylate segments with a well-defined molecular structure. When the resulting block copolymer is heated to 110 °C, a methacrylate homopolymer with the same molecular weight and molecular weight distribution as the macroinitiator used for polymerization is recovered. This finding indicates that only the polyperoxide segments are selectively decomposed by heating.

The block copolymer exhibits two T_g values due to both segments. The T_g of the polymethacrylate is low, and the 180° peel strength of the tape made using the block copolymer as the adhesive reaches a value more than twice that of commercially available adhesive tapes. As shown in Table 3, the peel strength decreases to approximately 5% when heated at 60 °C for 1 h, and spontaneous peeling is observed when heated at 100 °C for 1 h. A photograph of the sample before peeling shows that many air bubbles are generated at the interface between the tape and the adhesive after heating (Fig. 9). Interestingly, excellent adhesive properties are obtained by using the block copolymer, but stick–slip phenomena occur with each homopolymer and their blends. It has been revealed that these materials do not function adequately as adhesives (Table 3).

In addition, main-chain degradable polyperoxide gels and crosslinking point degradable polyperoxide gels have been developed to investigate their adhesion behaviors (Fig. 10). The adhesives containing crosslinked polyperoxide structures exhibit high breaking strength before heating, and the breaking strength decreases significantly after heat treatment.

Furthermore, the stability and heat resistance during use can be controlled by selecting the diene monomer used as the raw material. Polyperoxide that is synthesized from 2,4-hexadiene, i.e., PPHD, contains a 2,5-structure in its main chain repeating unit, which interrupts chain decomposition when used as adhesive materials (Table 3). This molecular design is effective for stabilizing polyperoxide materials; the effect of adding a thermally latent amine to further improve thermal stability has recently been demonstrated [87, 88].

Table 3 Changes in 180° peel strength of dismantlable adhesive tapes fabricated with polyperoxides as PSA[a] (ref. [83])

PSA	M_n	Heating conditions	180° peel strength (N/25 mm)	Relative strength (%)	Decrease in polymer weight after heating (wt.%)
PPMS	4000	None	Not determined (stick–slip)	-	-
P2EHMA	3400	None	Not determined (stick–slip)	-	-
PPMS/P2EHMA (polymer blend)	4000/3400	None	Not determined (stick–slip)	-	-
P2EHMA-b-PPMS	4900	None	13.3 ± 7.0	100	-
		50 °C for 1 h	1.8 ± 1.4	14	2.1
		60 °C for 0.5 h	1.1 ± 0.4	8	1.8
		60 °C for 1 h	0.68 ± 0.17	5	2.9
		100 °C for 1 h	~0	~0	30.5
P2EHMA-b-PPHD	6100	None	0.88 ± 0.20	100	-
		60 °C for 1 h	0.21 ± 0.10	24	0.5
		100 °C for 1 h	~0	~0	4.3

[a]With PET film and stainless-steel plate as the substrates. The peeling rate was 30 mm/min

(a) Change in adhesion strength
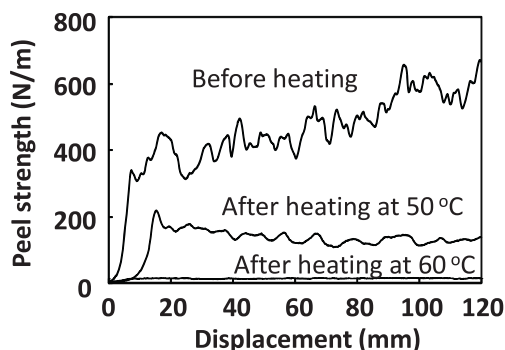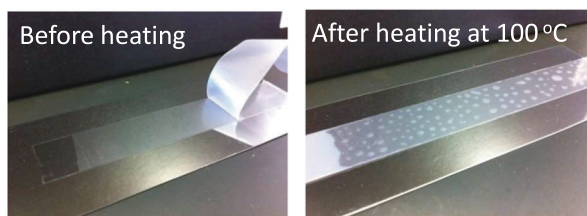

(b) Photograph of test specimens

Fig. 9 a Change in the peel strength of a block copolymer including a PPMS segment [poly(2EHMA-b-PPMS)] before and after heating at 50 and 60 °C for 1 h. The peel test is carried out with a PET film and SUS plate as the substrates at room temperature and a peeling rate of 30 mm/min. **b** Photographs of the test specimens before and after heating at 100 °C for 1 h. Many bubbles are observed after heating

Nonvinyl monomers other than oxygen are used to synthesize degradable polymers. Polysulfone is a polymer containing a sulfonyl group (–SO$_2$–) in its main chain. Aromatic polysulfone, a common aromatic polysulfone synthesized by polycondensation, has excellent heat resistance and is used as an engineering plastic. In contrast, poly(olefin sulfone)s, which are produced by alternating copolymerization of olefins with sulfur dioxide, are easily decomposed by heat, base, or electron beam irradiation [89, 90]. Poly(diene sulfone) with a 1,4-diene structure is obtained by radical copolymerization of diene monomers with sulfur dioxide [91]. For example, the analysis of IR and NMR spectra for polymers produced by radical copolymerization of butadiene, isoprene, and 2,4-hexadiene with sulfur dioxide reveal that alternating copolymers are produced and that the repeating units of the diene monomer are always controlled to the 1,4-addition with a high selectively. The DFT calculations reveal the reaction mechanism with a high regioselectivity during the propagation of diene monomers and sulfur dioxide, as shown in Table 4 and Fig. 11 [92, 93]. The sulfonyl radical R1 is selectively added to produce an allyl radical ($\Delta H_\alpha - \Delta H_\beta = -96$ to -98 kJ/mol), and the allyl radical favors the 2,5-addition to sulfur oxide rather than the 2,3-addition. The addition of the allyl radical is a reversible process, resulting in high selectivity via a mechanism similar to that for the alternating copolymerization of diene monomers and molecular oxygen (Table 2). Poly(diene sulfone)s are easily thermally decomposed by heating, but when the double bonds contained in the main chain of polydiene sulfones are hydrogenated, depolymerization is suppressed, and the thermal stability is improved. Poly(diene sulfone)s are expected to be used as heat-responsive and heat-resistant polymers according to the hydrogenation process during the post-polymerization reaction (Fig. 12) [92].

Recently, new types of polymerization reactions have been reported for the synthesis of degradable polymers by the radical copolymerization of nonvinyl monomers. Kamigaito et al. succeed in the synthesis of a polymer containing sulfur atoms in the main chain by the radical copolymerization of a thioamide derivative and a vinyl

Fig. 10 Synthesis and degradation of the dismantlable adhesion gels with high strength. **a** Main-chain degradable gel and (**b**) crosslinking point degradable gel
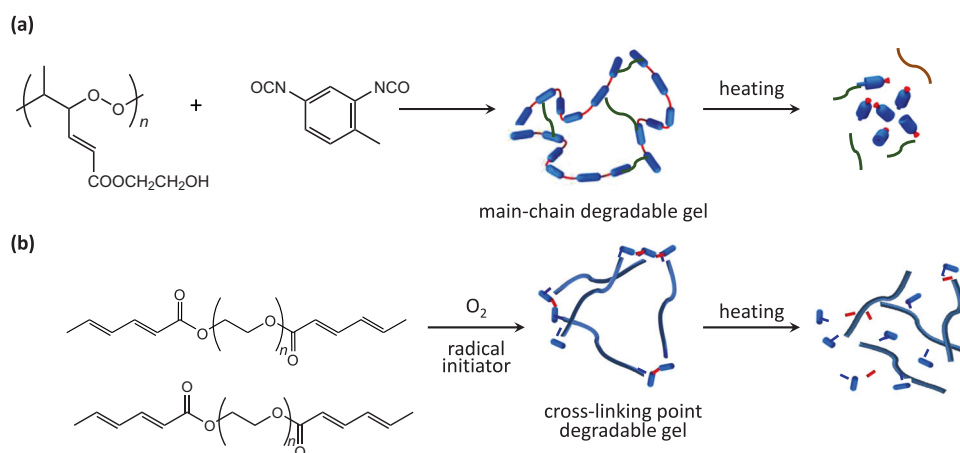

main-chain degradable gel

cross-linking point degradable gel

Table 4 DFT calculation results for an enthalpy change for the model cross-propagation reactions of 2,4-hexadiene (HD) and SO_2 (Fig. 11 for the structure and reactions of the radicals, from ref. [93])

Radical	Monomer	Addition	Product	ΔH (kJ/mol) [$\Delta\Delta H$ (kJ/mol)]		
				6-311 G (d, p)	6-311 + + G (3df, 3pd)	cc-pVTZ
R1	HD	α-	**R2a**	−23.47 [−97.11]	−11.76 [−95.86]	−18.16 [−98.49]
		β-	**R2b**	73.64	84.10	80.33
R2a	SO_2	2,5-	**R3a**	−9.29 [−14.23]	−1.76 [−14.85]	1.21 [−15.02]
		2,3-	**R3b**	4.94	13.10	16.23
R3a	HD	α-	**R4a**	−18.91 [−108.87]	−7.07 [−108.32]	−14.69 [−110.50]
		β-	**R4b**	89.96	101.25	95.81
R3b	HD	α-	**R4c**	−4.18 [−110.04]	7.36 [−108.11]	1.72 [−109.58]
		β-	**R4d**	105.86	115.48	111.29
R4a	SO_2	2,5-	**R5a**	−20.71 [−32.30]	−7.20 [−26.53]	−5.77 [−27.87]
		2,3-	**R5b**	11.59	19.33	22.09
R4c	SO_2	2,5-	**R5c**	−27.45 [−44.73]	−16.15 [−44.43]	−16.69 [−47.32]
		2,3-	**R5d**	17.28	28.28	30.63

monomer [94]. This copolymerization includes radical addition to the compound with a C = S bond. This sulfur-containing polymer is easily decomposed by the action of reducing agents, causing main-chain scission. Polymers containing sulfur atoms are synthesized by the ring-opening cationic polymerization of cyclic thioacetal monomers [95]. Furthermore, functional groups can be efficiently introduced into the main chain of the produced polymer when radical ring-opening polymerization is used [96]. In addition to nonvinyl monomers, cyclic monomers with molecular structures that combine a highly reactive double bond, such as an exomethylene group, are effective monomers for the synthesis of degradable polymers by radical copolymerization. Cyclic monomers used in radical ring-opening polymerization are classified into those with a vinyl group adjacent to the outside of the cyclic structure and those with an exo-type methylene group directly connected to the ring structure. These double bonds exhibit high reactivity depending on the structures of the surrounding substituents, and radical copolymerization with other vinyl monomers is

possible, in which a ring-opening reaction proceeds following radical addition. By introducing repeating units derived from these ring-opening polymerizable monomers into a part of common vinyl polymers, it is possible to impart degradability to vinyl polymers that are originally nondegradable [97]. Furthermore, there is a growing movement to find new methods for decomposing polymers by precisely controlling depolymerization using living radical polymerization [98]. The synthesis of degradable polymers using radical polymerization is one of the most important themes in the research field of polymer synthetic chemistry.

Dual-stimuli responsive dismantlable adhesive materials

As mentioned in the previous section, the use of polyperoxides is principally successful in providing degradable polymer materials, which can be used as dismantlable

Fig. 11 Regiospecific
propagation for the alternating
copolymerization of 2,4-
hexadiene with SO$_2$. For the
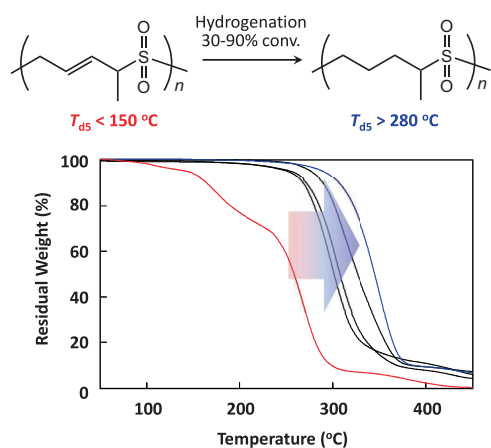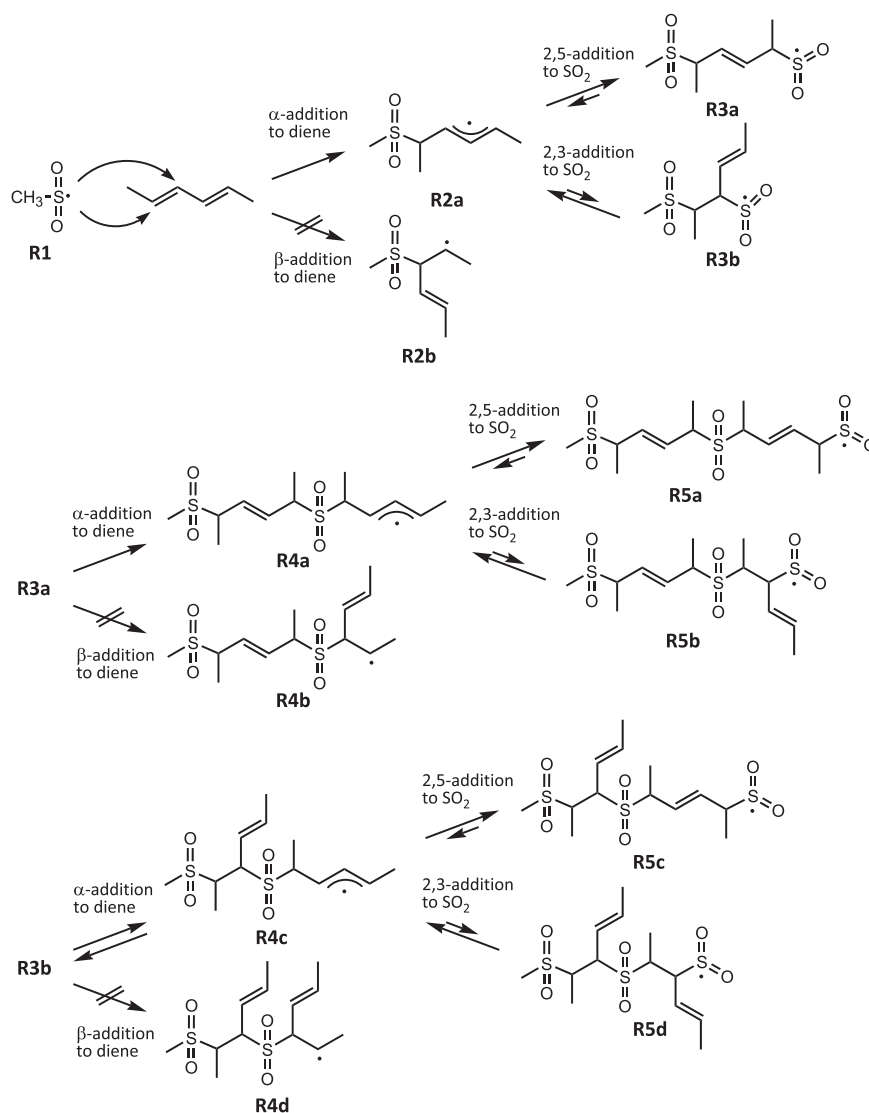results of the DFT calculations,
see Table 4

Fig. 12 Thermogravimetric curves for poly(diene sulfone) synthesized by the alternating copolymerization of 1,3-pentadiene and SO$_2$ and hydrogenated poly(diene sulfone)s. The hydrogenation conversions are 29.6, 49.2, 67.4, and 89.7%

adhesive materials. In addition, some important unresolved issues remain, such as the long-term storage stability and the safety of handling the material. Ideal dismantlable adhesive materials must ensure both reliable bond strength during use of the final product and rapid response to external stimuli, which are needed in operations to comply with the 5Rs (recycle, reuse, reduce, rework, and repair) (Fig. 13a). Additional understanding is needed to find a balance between these mutually contradictory conditions of stability during use and rapid disassembly.

We must conclude that when designing adhesive materials for future practical use, if we stick to systems that use polyperoxide, it is difficult to satisfy both stability during use and quick disassembly after use. We decide to make a drastic change in the direction of material design and proceed with development using a completely different type of reaction and material. In addition, to make practical application realistic, we decide to limit the materials used (not
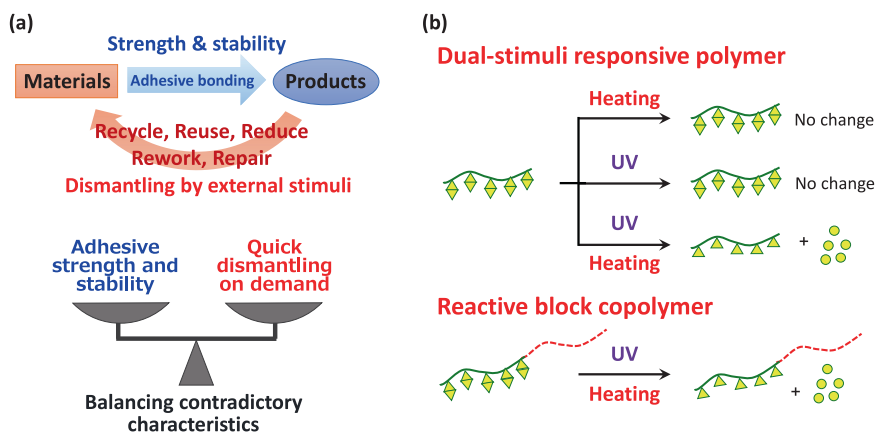
Fig. 13 a Factors needed for the development of dismantlable adhesive materials. Both adhesion strength and stability during use and quick response to external stimuli for an on-demand dismantling process should be considered for materials design. **b** Concept of dual-protected dismantlable adhesive materials. The materials that have no response to a single stimulus of heating or UV irradiation but quickly react by UV irradiation and postbaking are useful as dual-stimuli responsive adhesive materials. Furthermore, each sequence of the block copolymers is designed to have the functions of adhesion and response to stimuli for separate dismantling

Fig. 14 a Degradation of PtBA by UV irradiation and postbaking in the presence of PAG to yield PAA and isobutene.
b Photodecomposition mechanism of BCD and NIT used as PAG to yield sulfonic acids
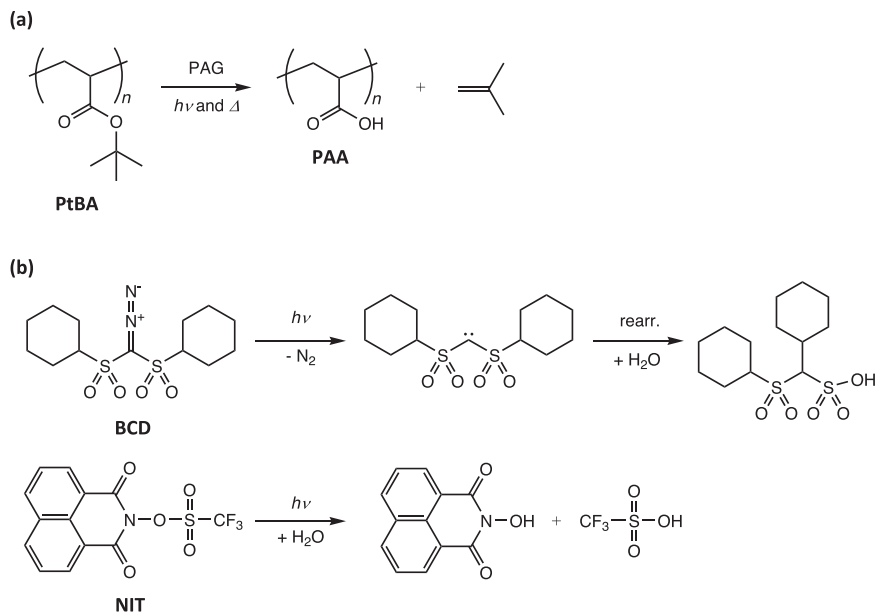
only polymers but also all other necessary materials) to those that are commercially available. After extracting the performance limits and issues of existing applied technologies in the related fields and examining various material design proposals on the desk in search of the ideal image of easily dismantlable adhesive systems, we can achieve both safety and disassembly. Eventually, we propose a new material design that selectively reacts when two types of stimuli are applied: a dual-stimuli responsive dismantlable adhesive system to achieve safety and degradability [99] (Fig. 13b).

The dual-stimuli responsive type of dismantlable adhesive system is explained using our specific examples of the systems. Poly(*tert*-butyl acrylate) (PtBA) is rapidly deprotected from its ester groups by heating in the presence of an acid catalyst to form poly(acrylic acid) (PAA) and isobutene (Fig. 14a). When gas is generated from the adhesive, it is expected that the cohesive force and adhesive area decrease, and the T_g and polarity of the polymer change significantly. When a photoacid generator (PAG) is added as a latent acid catalyst to this heat-responsive system, the external stimuli necessary for deprotection become the two steps of UV irradiation and postbaking (Fig. 14b). This two-step deprotection process has actually made it possible to achieve excellent heat resistance of the adhesive before acid generation and rapid disassembly through deprotection via
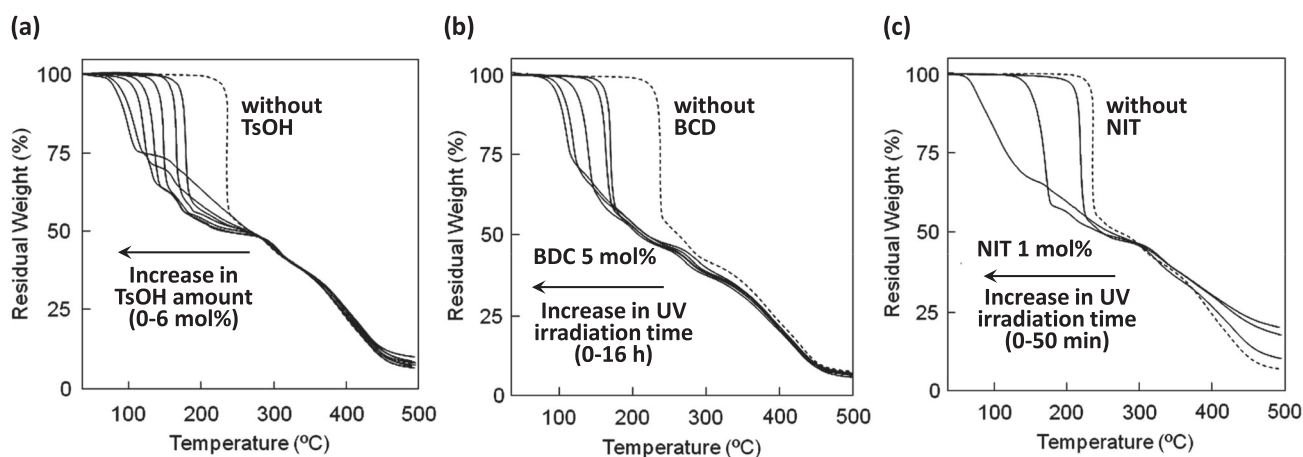
Fig. 15 Thermogravimetric curves for PtBA in the presence of (**a**) TsOH, (**b**) BCD, and (**c**) NIT at a heating rate of 10 °C/min in a nitrogen stream. The amount of added TsOH and the UV irradiation time are changed

irradiation and subsequent heating. The dual-stimulus response materials are stable to a single instance of heating or UV irradiation (Fig. 13b). However, it has been predicted from the beginning that it is not easy to molecularly design a material that can easily decompose and function well as an adhesive material. We determine that forcibly developing single materials is not an efficient method and decide to proceed with material development by actively utilizing block copolymers from the beginning of the process (Fig. 3). By using a block copolymer with microphase separation, we can fully exploit the physical properties of each segment contained in the polymer. In addition, there has been support in terms of the synthesis of block copolymers by the remarkable development of living radical polymerization (i.e., RDRP) technology in recent years. The range of selection of suitable polymerization methods and reaction conditions has expanded depending on the needed polymer structures and physical properties, i.e., the type of monomer used.

The conversion of PtBA to PAA accompanied by the elimination of isobutene proceeds even with heating alone (a high temperature over 200 °C), but in the presence of an acid catalyst, it can be performed under relatively mild temperature conditions (Fig. 15a) [99]. Adding a large amount of acid catalyst reduces stability; thus, it is difficult to control the reactivity through the amount of acid catalyst added and to achieve stability and a rapid response. Here, when PAG, such as bis(cyclohexyl sulfonyl)diazomethane (BDC) or *N*-trifluoromethylsulfonyl-1,8-naphthalimide (NIT), is added, the deprotection temperature decreases depending on the amount of PAG added and the UV irradiation time. The decomposition reaction of the polymer progresses, and disassembly becomes possible under gentle heating conditions (Fig. 15b, c). Since PAG generates an acid when irradiated with UV light, PtBA exists stably in

the dark. When BDC is used, a relatively large amount (several mol%) and long-term irradiation (several hours or more) are required to generate a sufficient amount of acid. When added in large amounts, there is a tendency for acid generation by heating alone, even without UV irradiation. In contrast, NIT generates a sufficient amount of strong acid (trifluoromethanesulfonic acid) within 1 h of irradiation when added in a small amount (1 mol%) and to efficiently convert PtBA to PAA.

The physical properties of the adhesive polymer are carefully controlled. The T_g of PtBA is 55 °C, which is overly high to be used as PSA; thus, we copolymerize *tert*-butyl acrylate (tBA) with *n*-butyl acrylate (nBA) and 2-ethylhexyl acrylate (2EHA). The T_g values of the adhesives are adjusted by controlling the compositions of the monomers used. Furthermore, to improve the cohesive force of the adhesive and increase its adhesion strength, we synthesize a copolymer incorporating 2-hydroxyethyl acrylate (HEA) units. Living radical polymerization is used to synthesize the adhesive, with the intention of precisely controlling the molecular weight and sequence structure. First, we synthesize a block copolymer for adhesives using ATRP [100–102], confirm how effective the idea shown in Fig. 13b is in practice, then start a series of experiments to develop new materials [99]. Next, to efficiently increase the molecular weight and introduce polar functional groups, we change the polymerization method from ATRP to organic tellurium-mediated living radical polymerization (TERP) for polymer synthesis [103, 104]. At that time, the only methods for preparing the organotellurium compounds used as polymerization control agents were synthesis in a laboratory using a dry box and individual supply. To date, some organic tellurium compounds are commercially available from a reagent manufacturing company in Japan for anyone as the general user.

Table 5 Changes in the 180° peel strengths of dismantlable adhesive tapes using tBA block copolymers.[a] (refs. [97, 101])

Polymers	NIT (mol%)	Photoirradiation and postheating conditions for dismantling	180° peel strength (N/20 mm)	Relative strength (%)	Failure mode
PtBA-b-P(tBA-co-2EHA) $[M_n = 2.11 \times 10^5]$	0.4	None	1.3	100	Cohesive
		UV/1 h, 100 °C/1 h	0.79	62	Cohesive
PtBA-b-P(tBA-co-2EHA-co-HEA) $[M_n = 2.58 \times 10^5]$	0.4	None	6.0 ± 0.3	100	Interfacial (SUS)
		100 °C/1 h	7.0 ± 1.2	117	Cohesive
		UV/1 h	8.9 ± 0.8	147	Interfacial (SUS)
		UV/1 h, 100 °C/1 h	0.35 ± 0.19	6	Cohesive
PtBA-b-P(tBA-co-2EHA-co-HEA) $[M_n = 2.03 \times 10^5]$	0.8	None	6.7 ± 1.8	100	Interfacial (SUS)
		UV/1 h, 100 °C/1 h	0.18 ± 0.19	3	Interfacial (PET)
P(tBA-co-2EHA-co-HEA) [random, $M_n = 2.32 \times 10^5$]	0.8	None	13.4 ± 3.7	100	Interfacial (SUS)
		UV/1 h, 100 °C/1 h	2.3 ± 0.7	17	Cohesive

[a]With PET film and stainless-steel plate as the substrates. The peeling rate is 30 mm/min

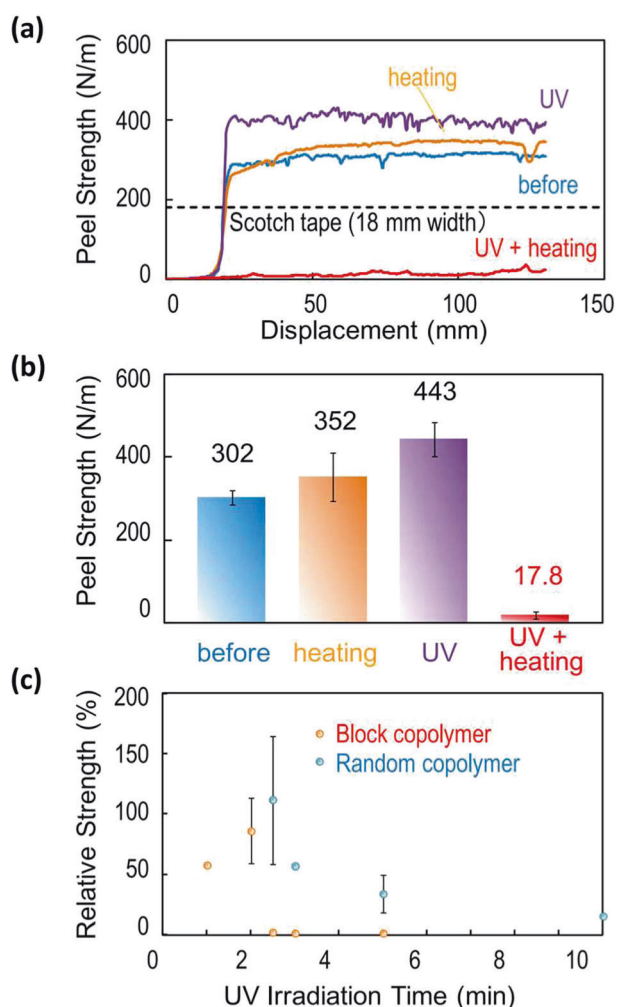**Fig. 16 a** Change in peel strength for the 180° peeling test of PtBA-b-poly(tBA-co-2EHA-co-HEA) in the presence of 0.4 mol% of NIT before and after UV irradiation and postbaking. **b** Comparison of the peel strength. **c** Comparison of the dismantlable adhesion property for quick response to external stimuli. UV irradiation for 1–10 min and postbaking at 150 °C for 5 min

We focus on the versatility of the polymerization control method using diphenyl ditelluride, which has excellent stability and is commercially available. Diphenyl ditelluride is a relatively stable compound that can be handled in air without the need for a special vacuum chamber. By simultaneously using an azo initiator, it is possible to generate organotellurium compounds as dormant species from diphenyl ditelluride during a living radical polymerization process [105]. We can control polymerization by using a combination of an azo initiator with a high decomposition rate to form dormant species and an azo initiator with a relatively low decomposition rate to sustainably generate the needed concentration of propagating radicals [106]. A block copolymer is synthesized by first polymerizing tBA and by then adding nBA (or 2EHA) and HEA. A molecular design that plays separate roles is used in which one segment has physical properties that change significantly in response to an acid and another segment functions as an adhesive [106–108].

Both a block copolymer and a random copolymer are synthesized, and the changes in peel strength due to external stimulation are compared (Table 5) [106]. Although NIT is added as PAG to the test piece in advance, the peel strength does not decrease by heating to 100 °C or UV irradiation alone. Conversely, heating the tape at 100 °C after UV irradiation reduces the peel strength to less than 10% of that of the untreated tape. This finding suggests that the use of PAG allows for two-step decomposition protection, in which it is stable against the stimulation of heating and light irradiation alone, but the reaction effectively proceeds when heated after UV irradiation (Fig. 16). In this system, deprotection, gas evolution, and formation of acrylic acid units promote dismantling. In addition, the introduction of the HEA unit not only improves peel strength during use but also reduces peel strength during disassembly. It has been revealed that deprotection of the tBA unit and

crosslinking by transesterification of the HEA unit function can synergistically reduce the peel strength upon disassembly [108].

Furthermore, in response to the desire to optimize disassembly work in the recycling process efficiently and quickly, the peeling performance within a few minutes is investigated (Fig. 16c). When the block copolymer is heated at 150 °C for 5 min after UV irradiation for 2.5 min, the relative peel strength decreases to approximately zero. In contrast, when the random copolymer is UV irradiated for 10 min and heated at 150 °C for 5 min, the strength does not decrease sufficiently [106]. The rate of the chemically amplified transformation of the *tert*-butyl ester to the carboxylic acid in the side chain accompanying the isobutene elimination [109] may be accelerated in the block copolymer sequence rather than in the random copolymers because of the high segment densities of the *tert*-butyl ester groups in the polymer (Fig. 20). Furthermore, interfacial failure is the dominant failure mode for adhesives using block copolymers. SEM observation of cross-sectional images of adhesive layers reveals that the tightly adhered interfaces of the random copolymer can transform pillar-like adhesives separated by void spaces between the PET support film and the stainless steel (SUS) plate after the dismantling treatment. A decrease in the cohesive force of the random copolymer can be rationalized by void formation. In contrast, ridge-shaped adhesives stuck to the SUS plate are observed for the block copolymer after the dismantling treatment. Void space exists between the PET support film and the adhesive, resulting in PET interfacial failure (Table 5) [110]. To further shorten the time required to dismantle adhesive tape, a light-emitting diode (LED) is used as the light source for disassembly within a few minutes. When UV irradiation is performed for 1 min under heating conditions of 130–150 °C, a rapid decrease in adhesion strength is confirmed [111].

We have investigated monomers other than tBA as reactive acrylate monomers used for the purpose of changing adhesive properties in response to various external stimuli. The use of acetal-protected acrylic acid makes it possible to change the disassembly conditions [112]. We succeed in simplifying the conditions for side-chain transformation of the acetal-protected polymer, that is, the conditions for disassembling the bonded material, such as immersion in hot water for 10 min or UV irradiation to the system with a small amount of NIT at room temperature. Under the light irradiation conditions for the acetal-protected adhesives, crosslinking progresses efficiently, and the adhesive layer gels without leaving adhesive residue on the adherend material or the supporting film. As a result, the flexible adhesive layer alone can be peeled off and completely separated from the adherend.

In this manner, in developing dismantlable adhesives that utilize the deprotection of acrylic esters, we achieve stability during use and the quickness of dismantling by controlling disassembly conditions, such as irradiation time and heating temperature, and by designing an adhesive material with dual protection. Additionally, the disassembly process is shortened. However, there are obstacles to the development of ideal dismantlable adhesive materials. Although the results of the material evaluation in the laboratory are satisfactory, there are issues with long-term durability assuming practical usage conditions. For example, when we evaluate the degree of deterioration of adhesive properties over several months at 85 °C and 85% humidity, changes in physical properties are unavoidable. This material would be used sufficiently within the range of selected applications, but we have decided to further modify the design. The aim of developing guidelines for dismantlable adhesive materials is as universal as possible. We reconsider the necessity and inevitability of using light as an external stimulus for dismantling.

BOC-containing polymers with stability and quick responsibility

Thus far, we have explained the characteristics of adhesive materials that can be easily dismantled using heat (i.e., degradable polyperoxides) and adhesive materials that can be dismantled using both light and heat (i.e., dual-stimuli responsive adhesives). Generally, adhesives have a unique usage environment in which the adhesive exists in a narrow space sandwiched between adherends. In most cases, it is difficult to directly irradiate the adhesive interface with light, except for temporarily fixing adhesive tapes for semiconductor manufacturing, where the adherend is transparent and allows the irradiation light to pass through. Therefore, we have begun searching for a dismantlable adhesive material that is stable to a certain temperature and can be dismantled rapidly and discontinuously in response to heating at a higher temperature. As a result of preliminary studies, we confirm that a polymer with a *tert*-butoxy carbonyloxy (BOC) group with a protected hydroxy group in the side chain is suitable for this purpose [113, 114]. The BOC group is one of the protecting groups used in the fields of organic synthetic chemistry and biomaterials for the quantitative protection of amino and hydroxy groups. It is rapidly deprotected in the presence of a strong acid, and therefore, polystyrene derivatives containing BOC groups in the side chain are used as chemically amplified resist materials [109].

We have developed designer functional polymers in which the hydroxy groups in the side chain are protected by BOC groups. First, the corresponding BOC-protected
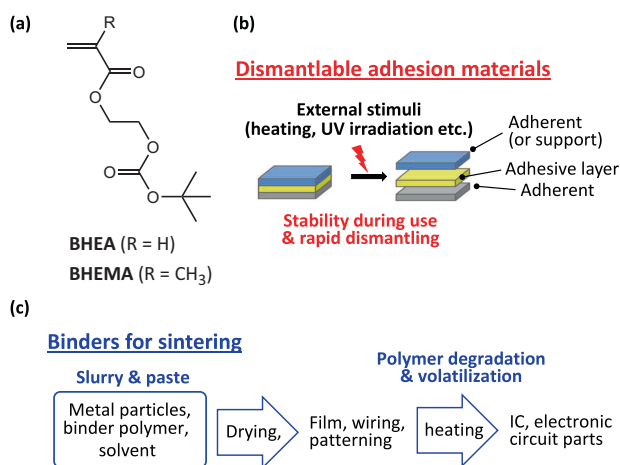
(a)

BHEA (R = H)
BHEMA (R = CH$_3$)

(b)

Dismantlable adhesion materials

External stimuli
(heating, UV irradiation etc.)

Adherent
(or support)
Adhesive layer
Adherent

**Stability during use
& rapid dismantling**

(c)

Binders for sintering

Slurry & paste

Metal particles,
binder polymer,
solvent

Drying,

Film, wiring,
patterning

**Polymer degradation
& volatilization**

heating

IC, electronic
circuit parts

Fig. 17 **a** Chemical structures of BHEA and BHEMA monomers developed for dismantlable adhesive materials. **b** Application as a PSA for dismantlable adhesion. **c** Application as degradable polymer binders used for the fabrication of semiconductor parts

Direct synthesis by polymerization ➡ Gelation

RAFT
polymerization

Protection   **Deprotection**

Polymer
reactions

Various
functional
polymers
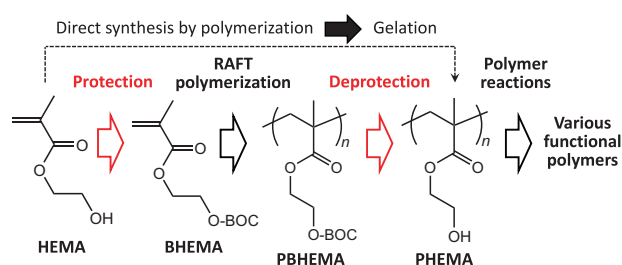
HEMA   BHEMA   PBHEMA   PHEMA

Fig. 18 Synthesis and polymerization of BHEMA and the deprotection of BOC groups in the side chain of the polymer of BHEMA to convert to the polymer of HEMA as the key material for functionalization of polymers

monomers derived from HEA [113] and 2-hydroxyethyl methacrylate (HEMA) [114], i.e., BHEA and BHEMA, respectively, are newly prepared, and then the reactive polymers are obtained by radical polymerization (Fig. 17a). The RAFT polymerization of BHEMA makes it possible to synthesize polymers, such as block copolymers with precisely controlled molecular weights, molecular weight distributions, end groups, and sequence structures [115] (Fig. 18). The copolymers containing BHEA repeating units with low T_g are useful as materials for dismantlable adhesive tapes (Fig. 17b), while the polymers derived from BHEMA are expected to be used as binder polymers for manufacturing electronic components (Fig. 17c).

To evaluate the properties of acrylic copolymers containing BHEA, 2EHA, and HEA as repeating units for dismantlable adhesive materials (Fig. 19a), the thermal decomposition behaviors of these copolymersare investigated using thermogravimetric analysis and IR spectroscopy [113]. The BHEA-containing polymer is stable upon heating at temperatures below 150 °C but rapidly decomposes when heated to 200 °C, releasing CO_2 and isobutene simultaneously upon deprotection of the *tert*-butoxycarbonyl group (Table 6). Typical thermogravimetric curves for the BOC-containing polymers, i.e., the homopolymers produced from 4-*tert*-butoxycarbonyloxystyrene (BSt), BHEA, and BHEMA, are shown in Fig. 20a. The deprotection process of the BOC group in the polymers can be tracked by IR spectroscopy and thermogravimetric analysis. When a change in the IR spectrum of the homopolymer of BHEA (**P1**) is monitored during heating at 200 °C using the polymer film cast on a silicon plate, the intensities of a peak due to the C = O stretching vibration of the carbonate group at 1738 cm^{-1} rapidly decrease according to the heating time within the initial several

minutes (Fig. 21a), and a broad absorption due to the O − H stretching vibration simultaneously appears at approximately 3400 cm^{-1}. On the basis of the peak intensity changes, the conversion of the BOC group to the hydroxy group is analyzed. As shown in the time−conversion curves for the homopolymers and copolymers (**P1** and **P2**s; Table 6 for the structure), the deprotection of the BHEA homopolymer occurs very fast, and the transformation is completely finished within 10 min. In contrast, the deprotection slowly proceeds for the copolymers, and the reaction rates depend on the BHEA contents in the copolymers. Such an acceleration of the deprotection rates depending on the BHEMA contents arises due to an autocatalytic reaction process, as previously reported for reactions including the deprotection and decomposition of several polymers [116–118]. An autocatalytic reaction is considered to be promoted by the interaction of an aliphatic hydroxy group produced by the deprotection, as shown in Fig. 19b. The weight-loss curves at a constant temperature in Fig. 21b support the contribution of an autocatalytic reaction mechanism for the deprotection of the BOC group. It should be noted that similar results can be observed for the thermogravimetric analysis under heating conditions at the constant heating rate shown in Table 6; the order of the T_{d5} values is **P2b** (195 °C) > **P3a** (194 °C) > **P3b** (177 °C) > **P3c** (170 °C), which agrees well with the content of the HEA repeating units in the copolymers (Table 6). An increase in the T_{d5} values for the **P2**s 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.

Shear retention power and 180° peel tests are conducted on the adhesive tapes using BHEA-containing copolymers. As a result, the copolymer containing 26, 35, and 39 mol% BHEA, 2EHA, and HEA units, respectively (**P3a**), exhibits a high adhesion strength (Table 7 and Fig. 20b). The adhesion strength rapidly decreases due to heating during the dismantling process. The addition of hexamethylene diisocyanate (HDI) as a crosslinking agent and Zn(acac)$_2$ as

Fig. 19 a Repeating structures of BHEA-containing acrylate random copolymers used as dismantlable adhesive materials (Table 6). **b** Autocatalytic effect on the thermal degradation of BHEA-containing polymers
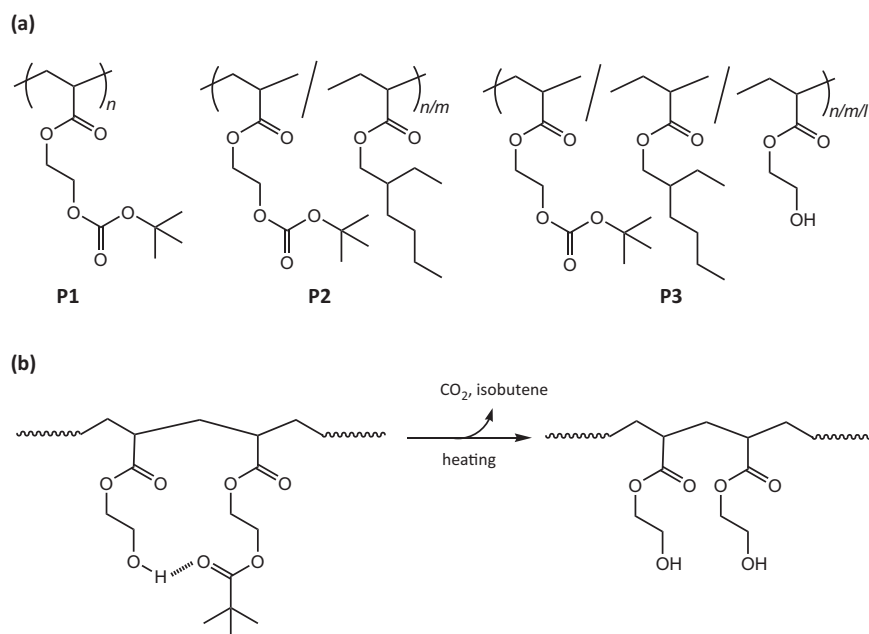

(a)

P1   P2   P3

(b)

CO_2, isobutene

heating

Table 6 Thermal properties of BHEA-containing acrylate random copolymers.[a] (ref. [113])

Polymer	[BHEA]/[2EHA]/[HEA] in copolymer (molar ratio)	M_n x 10^{-5}	T_g (°C)	T_{d5} (°C)	T_{max} (°C)	Residual weight after deprotection (%) [theoretical value]
P1	100/0/0	2.82	20	199	215	53.3 [53.7]
P2a	80/30/0	2.20	−13	191	224	65.1 [66.0]
P2b	50/50/0	1.96	−29	195	229	71.8 [75.0]
P2c	28/72/0	1.51	−61	225	219	84.8 [85.6]
P2d	19/81/0	1.60	−61	233	239	88.8 [89.9]
P2e	11/89/0	1.46	−64	239	243	91.5 [94.3]
P3a	38/38/14	2.72	−27	194	226	78.9 [79.6]
P3a[b]	38/38/14	2.72	-	150	224	76.0 [79.6]
P3b	26/35/39	6.32	−22	177	213	82.5 [84.5]
P3c	17/28/55	-	−18	170	208	87.1 [88.8]

[a]See Fig. 19a for the polymer structure. Tg was determined by DSC. Td5, Tmax, and the residual weights were determined by thermogravimetric analysis at the heating rate of 10 °C/min in a nitrogen stream

[b]In the presence of Zn(acac) 2 as the Lewis acid (3 mol%)

a Lewis acid to the adhesive polymer enables the design of high-performance dismantlable adhesive systems. The change in rheological properties during the dismantling process allows for rapid disassembly. Dynamic viscoelasticity measurements of the adhesive polymers clarify the effects of the elasticity of the adhesives on the adhesion strength and dismantling performance. The storage modulus (G') and loss modulus (G'') values are determined at angular frequencies of $0.06 - 200$ rad/s at room temperature before and after heating. As usual, a shear holding power is closely related to the viscoelastic property evaluated at a low angular frequency, while the peel behaviors of pressure-sensitive adhesive tapes are often discussed based on the dynamic mechanical parameters observed at a high angular

frequency greater than 102 rad/s. In Table 8, the G' and tanδ values determined at 0.0628 and 112 rad/s are summarized. The tanδ values are greater than unity at both frequencies before heating, indicating that the adhesive materials are typical viscous fluids. After heating at 200 °C for 40 min for the dismantling process, the G' values increase, and the tanδ values are less than unity because the adhesive polymers change from fluid to elastic states. Intermolecular hydrogen bonding between the HEA units produced by the thermal deprotection of the BOC groups contributes to an increase in the G' value. Thus, viscoelastic data supports efficient network formation by crosslinking due to the presence of the HEA repeating units in the copolymer. The crosslinking structure is confirmed by the determination of the insoluble
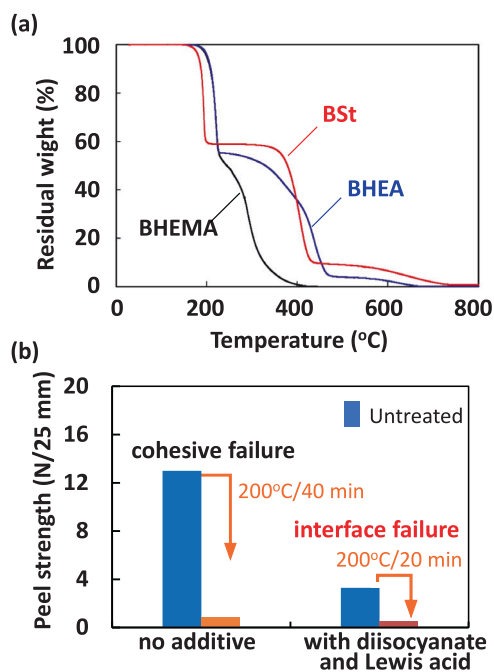
Fig. 20 a Thermogravimetric curves for the BOC-containing polymers produced from BHEA, BHEMA, and 4-(*tert*-butoxycarbonyloxy) styrene (BSt) at a heating rate of 10 °C/min in a nitrogen stream. **b** Change in peel strength for the 180° peeling test of BHEA-containing acrylate random copolymer (**P3a**) in the absence and presence of diisocyanate and Zn(acac)₂. See Table 7

fractions. The insoluble fraction reaches 59% after heating at 200 °C for 40 min.

For heat-responsive materials containing BOC groups, both stability in use and rapid degradability are needed. When heat is used as a single external stimulus, it is not possible to expect the distinctive on–off contrast seen in UV irradiation. This result occurs because the rate of a thermal reaction always proceeds according to the Arrhenius equation; thus, the reaction proceeds slowly even under relatively mild heating conditions. This phenomenon is the reason for the severe results in the long-term deterioration test at the final stage of the development of the dual-stimuli responsive dismantlable adhesive systems mentioned in the previous section. It is necessary to overcome the Arrhenius constraint, which can be achieved by using thermal latent acids (TLAs, also known as thermal acid generators) [119, 120]. TLAs are useful for designing heat-responsive polymers that react quickly upon heating and can clearly turn on and off with small temperature differences.

At a low temperature, TLA is in a protected state and does not function as an acid. For example, cyclohexyl *p*-toluenesulfonate (CHTS) and isopropyl *p*-toluenesulfonate (IPTS) are stable at room temperature and do not generate acids. When heated to 100 °C, deprotection, that is, the elimination of cyclohexene and propene, rapidly progresses, and *p*-

Fig. 21 a Change in IR spectrum for **P1** (left) and time–conversion curves for the deprotection of BOC groups for **P1** (black), **P2a** (red), **P2b** (blue), and **P2d** (green) (right). Heating at 200 °C on a silicon plate. **b** Thermogravimetric curves (left) and time–conversion curves (right) for the deprotection of BOC groups for **P1** (black), **P2a** (red), **P2b** (blue), and **P2d** (green) under isothermal conditions at 200 °C in a nitrogen stream. See Fig. 19a and Table 6 for the repeating unit structure of the polymers
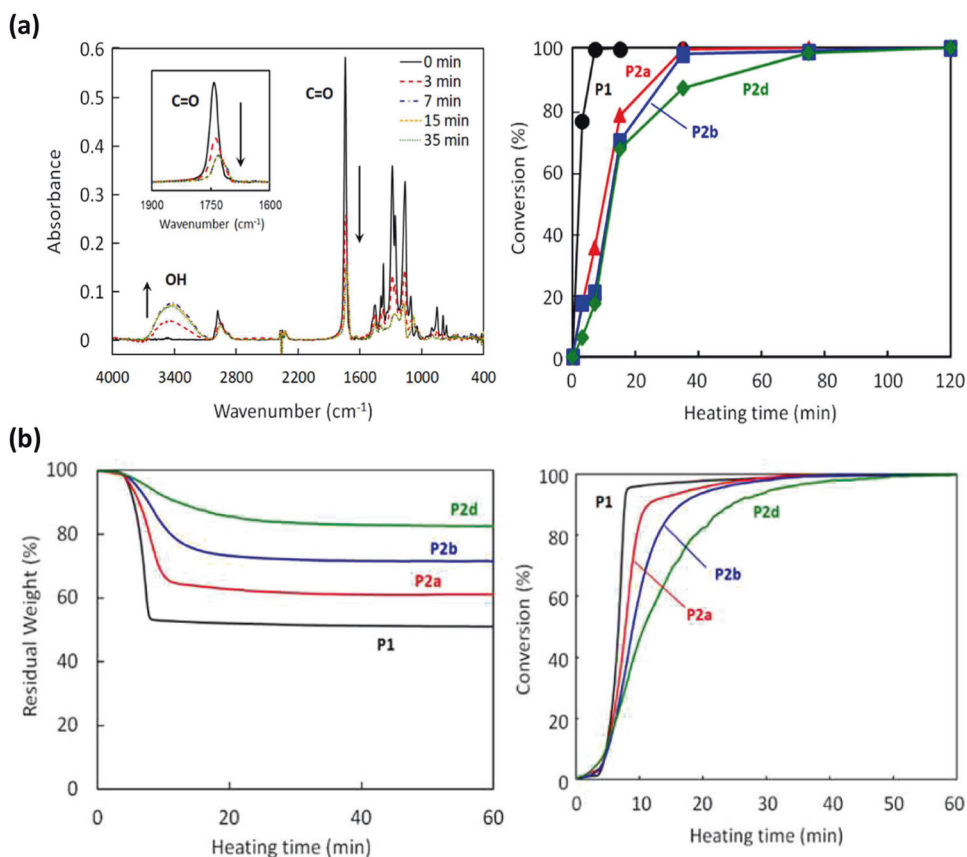
Table 7 Changes in 180° peel strength of BHEA-containing acrylate random copolymer (**P3a**) in the absence or presence of HDI and Zn(acac)₃[a] (from ref. [113])

| HDI (wt.%)	Zn(acac)₂ (wt.%)	Heating conditions for dismantling	180° peel strength (N/25 mm)	Relative strength (%)	Failure mode
5	0	None	9.54 ± 1.06	100	Interfacial
		200 °C for 40 min	6.07 ± 0.74	64	Cohesive
10	0	None	9.92 ± 1.26	100	Interfacial
		200 °C for 40 min	4.91 ± 1.73	49	Interfacial/Cohesive
0	3	None	4.47 ± 0.39	100	Interfacial
		200 °C for 5 min	4.60 ± 1.57	103	Cohesive
		200 °C for 10 min	1.44 ± 1.25	32	Cohesive
		200 °C for 20 min	0.56 ± 0.17	13	Cohesive
		200 °C for 40 min	0.28 ± 0.07	6	Cohesive
10	3	None	3.31 ± 0.53	100	Interfacial
		200 °C for 20 min	0.48 ± 0.11	15	Interfacial

[a]With PET film and stainless-steel plate as the substrates. The peeling rate is 30 mm/min

Table 8 Viscoelastic parameters determined for BHEA-containing copolymers at different angular frequencies (ref. [113])

Polymer	Heating conditions for dismantling	At 0.0628 rad/s		At 112 rad/s	
		G' (kPa)	tan δ	G' (kPa)	tan δ
P2b	None	1.39	1.93	96.3	1.22
	200 °C for 40 min	13.0	0.258	136	0.895
P3a	None	5.48	1.30	190	1.18
	200 °C for 40 min	408	0.606	3050	0.190

toluenesulfonic acid (TsOH) is produced (Fig. 22) [120]. The thermal deprotection of TLA is confirmed by thermogravimetric analysis, as shown in Fig. 23a. The produced TsOH efficiently functions as the acid catalyst for the deprotection of the BOC groups in the homopolymer of BHEMA (Fig. 23b). The onset temperature of the deprotection of the BOC group in the side chain of the BHEMA polymer drastically decreases by the addition of only 1 wt.% CHTS and IPTS as TLA. The effect of TLA addition on the dismantlable adhesive materials is summarized in Table 9, in which BHBA is used as the BOC-protected acrylate monomer derived from 4-hydroxybutyl acrylate (HBA). The deprotection of the BOC groups of the copolymers is accelerated, and the adhesion strength drastically decreases to less than 1% of the initial strength under heating conditions at 150 or 200 °C for 5–40 min in the presence of TLA. This phenomenon arises due to the promoting effect of the auto-catalytic reactions of TLA and BOC-protected groups. Consequently, the deprotection proceeds rapidly within a narrow temperature range, while the reaction hardly progresses below 100 °C. In this manner, we can realize a system that combines the stability and reactivity of BHEMA and BHEA polymers against the thermal response.

By combining BOC groups and TLA, we have succeeded in designing a new polymer material that exhibits a
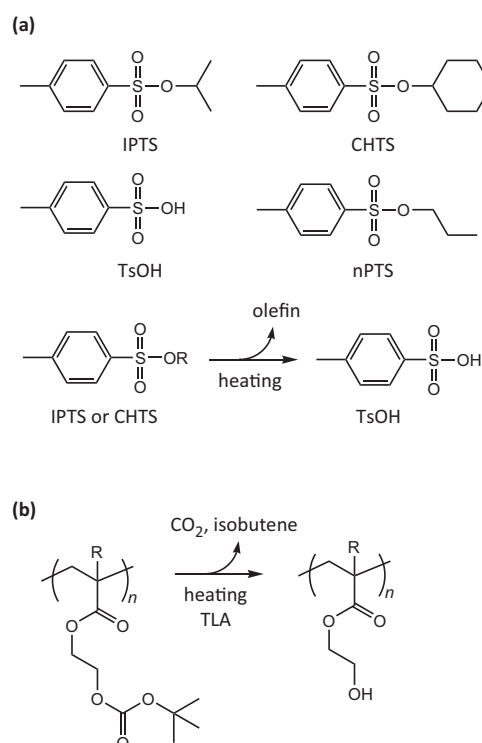
Fig. 22 a Chemical structures of IPTS and CHTS as the TLA, TsOH as the acid catalyst, and nPTS, and the deprotection of IPTS and CHTS to produce TsOH by heating. **b** Deprotection of the BOC group in the side chain of the polymers of BHEMA (R = CH₃) and BHEA (R = H) by heating in the presence of TLA to yield the polymers of HEMA and BHEA

sharp temperature response and in creating easily dismantlable adhesive materials that are stable during use and can be quickly dismantled using thermal stimulation. A method of combining two or more types of reactions is valid for the control of on and off switching because a product of one reaction can trigger and accelerate another reaction (Fig. 24). Such a reaction is expected to be applicable not
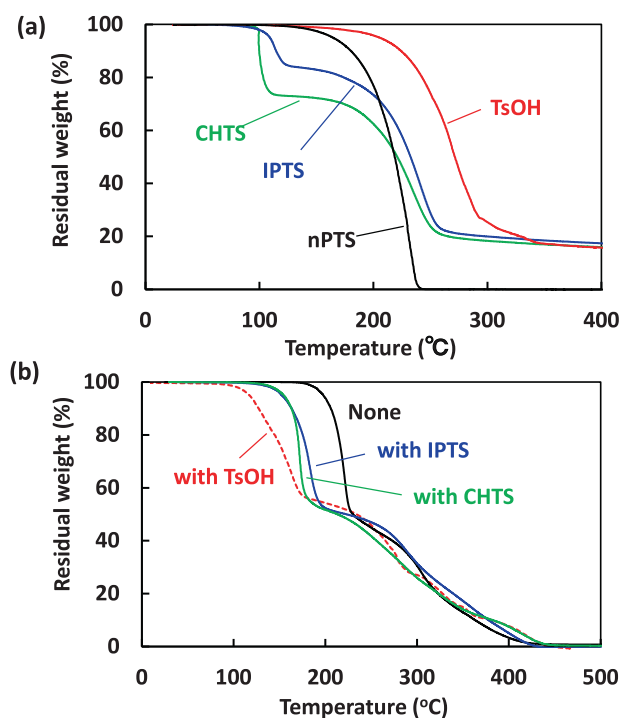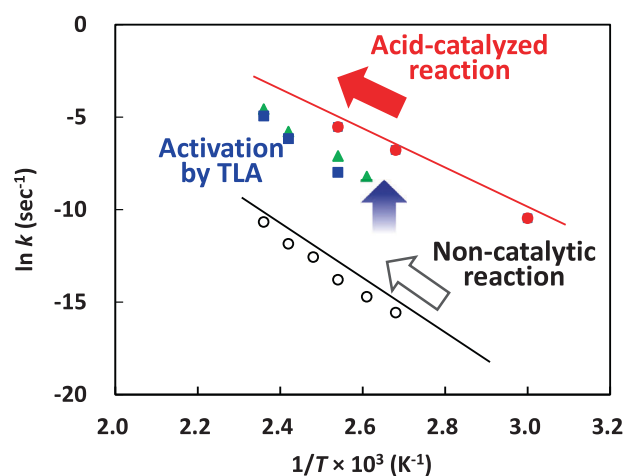
Fig. 24 Arrhenius plots for the deprotection rates of the polymer of BHEMA in the presence of IPTS (■), CHTS (▲), and TsOH (●) and in the absence of an additive (○)

Fig. 23 a Thermogravimetric curves for IPTS and CHTS as the TLA via a two-step decomposition mechanism (deprotection of a sulfonyl ester), which is different from the curves observed for TsOH and nPTS. b Thermogravimetric curves for the polymer of BHEMA in the absence and presence of IPTS, CHTS, and TsOH (1 wt.%). The heating rate is 10 °C/min in a nitrogen stream

Table 9 Changes in 180° peel strength of dismantlable adhesive tapes using poly(BHBA-co-2EHA-co-HBA) in presence of TLA[a] (from ref. [119])

Polymers	TLA[a] (wt.%)	Heating conditions for dismantling		180° peel strength	Relative strength
		Temp. (°C)	Time (min)	(N/25 mm)	(%)
Poly(BHBA-co-2EHA-co-HBA) [BHBA]/[2EHA]/[HBA] = 59/19/22	CHTS (0.5)	200	0	16.3 ± 1.6	100
		200	5	0.41 ± 0.08	2.5
		200	10	0.34 ± 0.03	2.1
		200	20	0.16 ± 0.06	< 1
		150	20	8.20 ± 0.53	50
		150	30	2.76 ± 1.25	17
		150	40	0.58 ± 0.02	3.5
	CHTS (1.0)	200	5	0.11 ± 0.04	< 1
		200	10	0.09 ± 0.06	< 1
		200	20	0.07 ± 0.02	< 1
Poly(BHBA-co-2EHA-co-HBA) [BHBA]/[2EHA]/[HBA] = 49/19/32	IPTS (1.0)	200	0	37.6 ± 0.1	100
		200	10	0.53 ± 0.03	1.4
		200	20	0.23 ± 0.08	< 1

[a]HBA 4-hydroxybutyl acrylate, BHBA BOC-protected HBA, CHTS cyclohexyl p-toluenesulfonate, IPTS isopropyl p-toluenesulfonate

only to dismantlable adhesive materials but also to a variety of materials and reaction designs in the future.

Conclusions

Among a variety of functions of adhesive materials, dismantlable adhesion, i.e., on-demand debonding, was the focus, and recent studies on heat-responsive adhesive materials used for dismantlable adhesive systems were described in this review article. The dual-stimuli-responsive dismantlable adhesive system using both light and heat stimuli further evolved into a BOC-protected adhesive system with TLA, exhibiting high-performance responsivity to a single thermal stimulus with excellent temperature sensitivity (Fig. 25). Another important function needed for adhesive materials is dissimilar material bonding, which has difficulty overcoming unsolved problems [121–125]. However, dissimilar material bonding is indispensable for sustainable material circular systems and lowered environmental negative impacts. Although there are still many difficulties, we hope that a new adhesive bonding system that combines both methods, i.e., dissimilar material bonding and dismantlable adhesive systems, will become a reality in the near future. There is a need to minimize the negative impact on energy and the environment in terms of raw materials and the manufacturing process, including usage environment, reuse, and final disposal. To increase the total efficiency, it is necessary to advance comprehensive efforts that include not only what materials to use but also systems for their utilization. We hope that the strong support of adhesives, which connect things, will create new materials in an infinite number of combinations from limited materials.
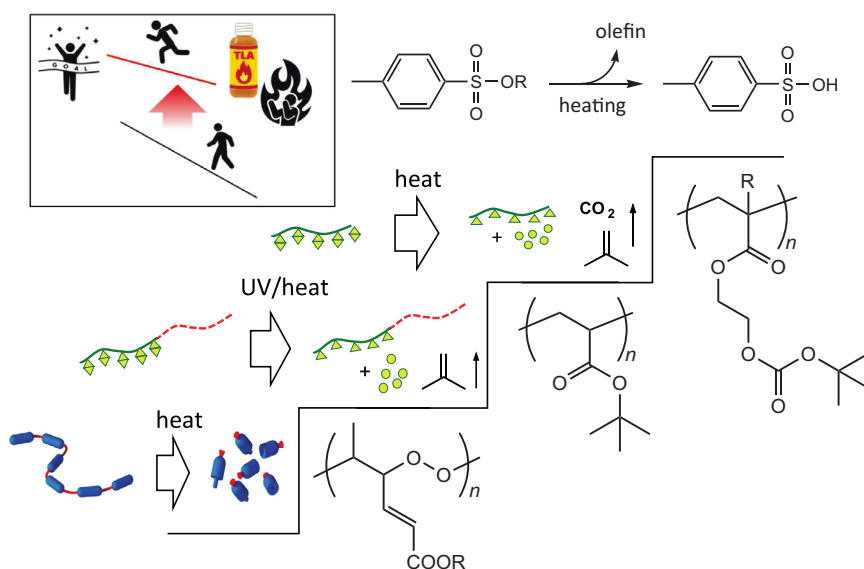
Fig. 25 Illustrative representation of the development of heat-responsive adhesive materials that are stable during use and quickly deteriorate during dismantling. The development first started from the synthesis of dismantlable adhesive materials using polyperoxides in the early material design and then evolved to dual-stimuli responsive materials, providing a guideline of material design for achieving stability during use and degradability during dismantling. Finally, heat-responsive dismantlable adhesive systems, which are thermally stable during use while responding quickly during disassembly by the use of the BOC group and the protected trigger TLA

Compliance with ethical standards

Conflict of interest The author declares no competing interests.

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