Polymer 99 (2016) 83–89

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Epoxy resin bearing diacylhydrazine moiety as a degradable adhesive for traceless oxidative removal

Takahiro Oguri, Akie Kawahara, Nobuhiro Kihara*

Department of Chemistry, Faculty of Science, Kanagawa University, Tsuchiya, Hiratsuka 259-1293, Japan

ARTICLE INFO

Article history:
Received 3 May 2016
Received in revised form
24 June 2016
Accepted 28 June 2016
Available online 2 July 2016

Keywords:
Oxidatively degradable polymer
Epoxy resin
Adhesive

ABSTRACT

Bisphenols functionalized with diacylhydrazine moieties and ester groups were prepared from 5-hydroxyisophthalic acid by esterification and partial hydrazination, followed by oxidative coupling of the obtained hydrazide. Ester groups with long alkyl chains or polyether increased the solubility of bisphenols in the epoxy resin. The epoxy resin was cured by heating with bisphenols in the presence of a catalytic amount of imidazole, with more rapid curing observed for more soluble bisphenols. The cured resin, with $T_{d5} \approx 300\ ^\circ\mathrm{C}$, decomposed rapidly when exposed to sodium hypochlorite solution. The above resin could be used as a strong and tough adhesive for metal and glass, whereas it can be easily removed by treatment with sodium hypochlorite solution without any trace. The observed dismantling rate positively correlated with bisphenol solubility.

1. Introduction

Adhesives should have two opposite properties: sufficient bonding strength during use and their amenable removal after use. Even though bonding strength has been conventionally given more importance, novel functional adhesives that lose their strength in response to external stimuli on demand have been extensively studied. Among such stimuli, photo-irradiation [1–5] and heating [6–12] have been widely studied, causing decomposition or polymerization of certain functional groups and the associated loss of adhesive strength. Thermal expansion of microcapsules is another principle for formulating thermally removable adhesives [13,14]. Acid-catalyzed isomerization or decomposition of ester or acetal groups has also been studied as dismantling stimuli [15–20]. Electrolysis is another dismantling stimulus that can be used [21,22]. Electrostatic interaction between ionic surfaces can be attenuated by the treatment with salt or hot water [23,24]. However, removing an adhesive from a material surface without leaving any residue is generally difficult when the adhesive exhibits strong bonding. Furthermore, since the stimuli utilized for dismantling, e.g., light, heat, acids, and water, are naturally ubiquitous, accidental dismantling may happen. Since sensitive dismantling requires a low threshold, amenable removal is incompatible with weather resistance.

We have reported poly(diacylhydrazine) as an oxidatively degradable polymer [25–28]. When diacylhydrazine is oxidized by certain oxidants such as sodium hypochlorite, the corresponding carboxylic acid and nitrogen gas are formed rapidly and quantitatively after hydrolysis. However, diacylhydrazine is inert to oxygen even at 300 °C. Poly(diacylhydrazine), a class of polyamide, is thermally and chemically (excluding specific oxidants) as stable as polyamide (nylon), a typical engineering plastic. Since sodium hypochlorite is an easily available but nonnatural compound, poly(diacylhydrazine) exhibits both high weather resistance and high degradability. These special features of poly(diacylhydrazine) prompted us to introduce the diacylhydrazine moiety into adhesives (Scheme 1).

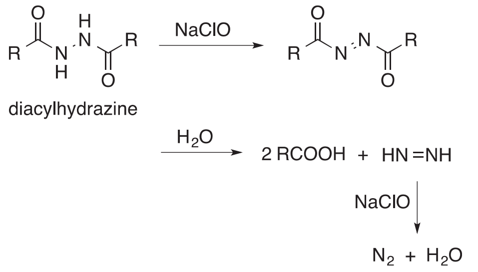
Among the various adhesives, we paid especial attention to epoxy resins, one of the strongest and toughest adhesives [29,30]. Epoxy resins are polyaddition-type polymers, and hence, the diacylhydrazine moiety can be introduced on the polymer backbone. Epoxy resins can be cured by bifunctional nucleophiles such as bisphenols in the presence of catalysts such as imidazole. Thus, bisphenols bearing the diacylhydrazine moiety can act as curing agents for epoxy resins, and the resins cured with such bisphenols are expected to be oxidatively degradable (Scheme 2).

In this paper, preparation of novel bisphenols with diacylhydrazine moiety is described. Curing of epoxy resins and oxidative degradation of the cured resin were examined. Furthermore, the use of the cured resin as an adhesive and its traceless oxidative

---

* Corresponding author.
E-mail address: kihara@kanagawa-u.ac.jp (N. Kihara).

http://dx.doi.org/10.1016/j.polymer.2016.06.066
0032-3861/© 2016 Elsevier Ltd. All rights reserved.



Scheme 1.

removal were studied.

2. Experimental section

2.1. General

NMR spectra were recorded on a JEOL JNM-ECP300, a JNM-ECA400, a JNM-ECS400, a JNM-ECP500, and a JNM-ECZ600 spectrometers using tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. Thermal gravimetric analysis (TGA) was performed on a Rigaku Thermo plus TG-8120 instrument using an aluminum pan under air. Differential scanning calorimetry (DSC) was performed on a RIGAKU Thermo plus DSC-8230 using a crimped aluminum pan under air. Tension was measured using an Instron 5565 Tester. All chemicals and solvents were reagent grade, and were used without further purification.

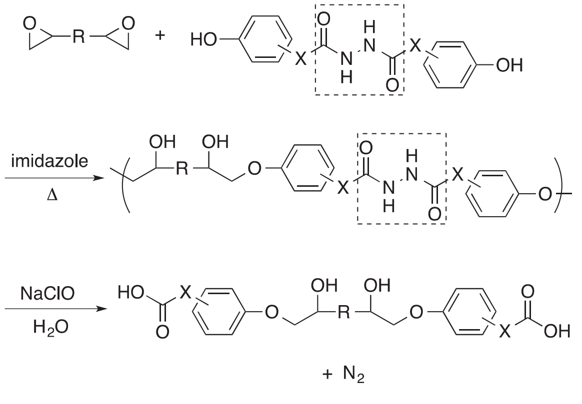
2.2. 10Et

A solution of 5-hydroxyisophthalic acid (6.17 g, 33.8 mmol) and *p*-toluenesulfonic acid monohydrate (2.38 g, 14 mmol) in ethanol (800 mL) was refluxed for 2 days. After the removal of the solvent *in vacuo*, the residue was dissolved in ethyl acetate, washed with sodium bicarbonate solution and brine, dried over magnesium sulfate, and evaporated to give **10Et** (7.92 g, 100%) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ 10.29 (s, 1H), 7.95–7.93 (m, 1H), 7.57 (d, $J = 1.4$ Hz, 2H), 4.32 (q, $J = 7.1$ Hz, 4H), 1.32 (t, $J = 7.1$ Hz, 6H) ppm.

2.3. 10Bu

A solution of 5-hydroxyisophthalic acid (5.01 g, 27.5 mmol) and *p*-toluenesulfonic acid monohydrate (712 mg, 3.74 mmol) in butan-1-ol (350 mL) was refluxed for 3 days. After the removal of the solvent *in vacuo*, the residue was dissolved in ethyl acetate, washed with sodium bicarbonate solution and brine, dried over magnesium sulfate, and evaporated to give **10Bu** (8.10 g, 100%) as a brown solid.



Scheme 2.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.30 (s, 1H), 7.94 (t, $J = 1.5$ Hz, 1H), 7.57 (d, $J = 1.5$ Hz, 2H), 4.28 (t, $J = 6.5$ Hz, 4H), 1.75–1.64 (m, 4H), 1.49–1.36 (m 4H), 0.94 (t, $J = 7.3$ Hz, 6H) ppm.

2.4. 10Oc

A solution of 5-hydroxyisophthalic acid (21.81 g, 120 mmol), octan-1-ol (40 mL, 437 mmol), and *p*-toluenesulfonic acid monohydrate (3.45 g, 18.1 mmol) in toluene (70 mL) was refluxed with Dean-Stark apparatus for 3 days. After the removal of the solvent *in vacuo*, the residue was dissolved in ethyl acetate, washed with sodium bicarbonate solution and brine, dried over magnesium sulfate, and evaporated to give **10Oc** (47.57 g, 98%) as an off-white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.30 (s, 1H), 7.94 (t, $J = 1.5$ Hz, 1H), 7.56 (d, $J = 1.5$ Hz, 2H), 4.27 (t, $J = 6.5$ Hz, 4H), 1.76–1.65 (m, 4H), 1.46–1.18 (m, 20H), 0.90–0.80 (m, 6H) ppm.

2.5. 10PE

A solution of 5-hydroxyisophthalic acid (40.18 g, 221 mmol), 2-(2-methoxyethoxy)ethanol (40 mL, 340 mmol), and *p*-toluenesulfonic acid monohydrate (4.14 g, 21.8 mmol) in toluene (50 mL) was refluxed with Dean-Stark apparatus for 3 days. After the removal of the solvent *in vacuo*, the residue was dissolved in ethyl acetate, washed with sodium bicarbonate solution and brine, dried over magnesium sulfate, and evaporated to give **10PE** (85.24 g, 100%) as a pale yellow oil.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.35 (s, 1H), 7.96 (t, $J = 1.6$ Hz, 1H), 7.59 (d, $J = 1.6$ Hz, 2H), 4.43–4.37 (m, 4H), 3.78–3.72 (m, 4H), 3.62–3.56 (m, 4H), 3.48–3.42 (m, 4H), 3.24 (s, 6H) ppm.

2.6. 11Et

A solution of **10Et** (37.61 g, 161 mmol) and hydrazine monohydrate (7.9 mL, 160 mmol) in ethanol (50 mL) was stirred for 3 days. The reaction mixture was poured into water, and the precipitate was collected by filtration, washed with water followed by ethyl acetate, and dried *in vacuo* to give **11Et** (18.07 g, 50%) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.08 (s, 1H), 9.87 (s, 1H), 7.85 (t, $J = 1.5$ Hz, 1H), 7.48–7.43 (m, 2H), 4.49 (s, 2H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H) ppm.

2.7. 11Bu

A solution of **10Bu** (1.17 g, 3.98 mmol) and hydrazine monohydrate (0.2 mL, 4.1 mmol) in ethanol (20 mL) was stirred at 40 °C for 2 days. The reaction mixture was poured into water, and the precipitate was collected by filtration, washed with water followed by ethyl acetate. The crude product was dissolved in methanol. Silicagel was added, and the solvent was evaporated *in vacuo* to charge the products on the silicagel. The products were chromatographed (eluent: dichloromethane-methanol, 40/1, v/v) to give **11Bu** (386 mg, 38%) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ 10.10 (s, 1H), 9.88 (s, 1H), 7.85–7.84 (m, 1H), 7.48–7.46 (m, 1H), 7.45–7.43 (m, 1H), 4.53 (s, 2H), 4.26 (t, $J = 6.4$ Hz, 2H), 1.73–1.64 (m, 2H), 1.47–1.37 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H) ppm.

2.8. 11Oc

A solution of **10Oc** (19.98 g, 49.1 mmol) and hydrazine monohydrate (2.4 mL, 49.4 mmol) in ethanol (30 mL) was stirred at 40 °C for 2 days. The reaction mixture was poured into ether, and the precipitate was collected by filtration. The crude product was dissolved in methanol. Silicagel was added, and the solvent was evaporated *in vacuo* to charge the products on the silicagel. The products were chromatographed (eluent: dichloromethane-methanol, 30/1, v/v) to give **11Oc** (7.28 g, 48%) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.10 (s, 1H), 9.88 (s, 1H), 7.86–7.82 (m, 1H), 7.48–7.42 (m, 2H), 4.54 (s, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 1.75–1.63 (m, 2H), 1.45–1.15 (m, 10H), 0.88–0.78 (m, 3H) ppm.

2.9. 11PE

A mixture of **10PE** (37.24 g, 96.4 mmol) and hydrazine monohydrate (4.8 mL, 99 mmol) was stirred for 3 days. The reaction mixture was dissolved in methanol. Silicagel was added, and the solvent was evaporated *in vacuo* to charge the products on the silicagel. The products were chromatographed (eluent: dichloromethane-methanol, 50/1, v/v) to give **11PE** (13.05 g, 48%) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.13 (s, 1H), 9.88 (br, 1H), 7.85 (t, *J* = 1.4 Hz, 1H), 7.49–7.46 (m, 1H), 7.46–7.43 (m, 1H), 4.50 (d, *J* = 3.9 Hz, 2H), 4.41–4.36 (m, 2H), 3.77–3.72 (m, 2H), 3.62–3.56 (m, 2H), 3.48–3.43 (m, 2H), 3.23 (s, 3H) ppm.

2.10. 12Et

To a mixture of acetonitrile (3.5 mL), water (3.5 mL), and NMP (3.5 mL) was dissolved **11Et** (1.31 g, 5.83 mmol), and Oxone (3.59 g, 5.84 mmol) was added. After stirring for 3 days, the reaction mixture was poured into water. The precipitate was collected by filtration, washed with water, dried *in vacuo* to give **12Et** (1.21 g, 100%) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ 10.64 (s, 2H), 10.23 (s, 2H), 7.96 (s, 2H), 7.54 (s, 4H), 4.34 (q, *J* = 7.1 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.16, 166.03, 158.68, 135.39, 132.45, 120.00, 119.79, 62.01, 15.12 ppm. IR (KBr): 3560, 3491, 3246, 3007, 1707, 1638, 1593, 1513, 1452, 1394, 1372, 1331, 1306, 1283, 1248, 1219, 1109, 1027, 1002, 980, 883, 796, 774, 721, 506 cm^{-1}.

2.11. 12Bu

To a mixture of acetonitrile (1.5 mL), water (1.5 mL), and NMP (1.5 mL) was dissolved **11Bu** (268 mg, 1.06 mmol), and Oxone (701 mg, 1.14 mmol) was added. After stirring for 2 days, the reaction mixture was poured into water. The precipitate was collected by filtration, washed with water, dried *in vacuo* to give **12Bu** (244 mg, 98%) as a pale yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ 10.66 (s, 2H), 10.27 (s, 2H), 7.96–7.93 (m, 2H), 7.56–7.52 (m, 4H), 4.30 (t, *J* = 6.5 Hz, 4H), 1.74–1.67 (m, 4H), 1.48–1.39 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 6H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.16, 165.99, 158.66, 135.38, 132.39, 119.97, 119.73, 65.62, 31.16, 19.69, 14.56 ppm. IR (KBr): 3304, 2961, 2874, 1721, 1697, 1648, 1592, 1559, 1496, 1445, 1394, 1332, 1251, 1110, 1061, 999, 984, 889, 772, 739, 674, 588, 555 cm^{-1}.

2.12. 12Oc

To a mixture of acetonitrile (3.5 mL), water (3.5 mL), and NMP (3.5 mL) was dissolved **11Oc** (1.59 g, 5.17 mmol), and Oxone (3.19 g, 5.20 mmol) was added. After stirring for 2 days, the reaction mixture was poured into water. The precipitate was collected by filtration, washed with water, dried *in vacuo* to give **12Oc** (1.41 g, 93%) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.64 (s, 2H), 10.21 (s, 2H), 7.97–7.92 (m, 2H), 7.57–7.51 (m, 4H), 4.29 (t, *J* = 6.3 Hz, 4H), 1.78–1.65 (m, 4H), 1.46–1.18 (m, 20H), 0.92–0.81 (m, 6H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.23, 166.06, 158.75, 135.43, 132.44, 120.06, 119.84, 65.93, 32.24, 29.67, 29.63, 29.18, 26.47, 23.08, 14.89 ppm. IR (KBr): 3428, 3306, 2955, 2925, 2855, 1719, 1696, 1589, 1559, 1496, 1391, 1332, 1243, 1105, 998, 984, 889, 773, 756, 737, 674, 654, 605 cm^{-1}.

2.13. 12PE

To a mixture of ethanol (20 mL) and methanol (20 mL) was dissolved **11PE** (4.26 g, 15.1 mmol), and PhI(OAc)$_2$ (4.87 g, 15.1 mmol) was added. After stirring at 50 °C for 2 days, the solvent was evaporated *in vacuo*. The residue was dissolved in methanol. Silicagel was added, and the solvent was evaporated *in vacuo* to charge the products on the silicagel. The products were chromatographed (eluent: dichloromethane-methanol, 20/1, v/v) to give **12PE** (3.29 g, 77%) as a pale yellow gummy solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.65 (s, 2H), 10.25 (s, 2H), 7.96 (t, *J* = 1.4 Hz, 2H), 7.55 (d, *J* = 1.4 Hz, 4H), 4.44–4.37 (m, 4H), 3.78–3.72 (m, 4H), 3.62–3.56 (m, 4H), 3.48–3.42 (m, 4H), 3.24 (s, 6H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.39, 166.32, 158.92, 135.62, 132.47, 120.32, 120.18, 72.42, 70.85, 69.51, 65.49, 59.18 ppm. IR (KBr): 3231, 2945, 1718, 1643, 1597, 1527, 1443, 1334, 1308, 1251, 1105, 1036, 1000, 978, 960, 884, 871, 846, 777, 755, 675, 613, 540, 501 cm^{-1}.

2.14. Curing

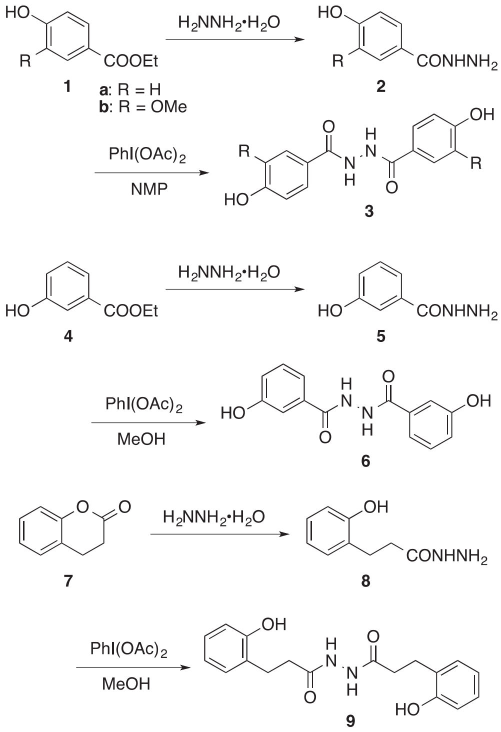
The epoxy resin was heated with an equimolar amount of bisphenol at 70–130 °C to prepare a homogeneous mixture. When the bisphenol did not completely dissolve in the epoxy resin even at 130 °C, the minimum amount of *N*-methylpyrrolidinone (NMP) was added to make the mixture homogeneous. Imidazole (10 mol% with respect to the epoxy resin) was added to the mixture, which was allowed to stand at the above temperature for 30 min to obtain the cured resin.

2.15. Adhesion and oxidative dismantling

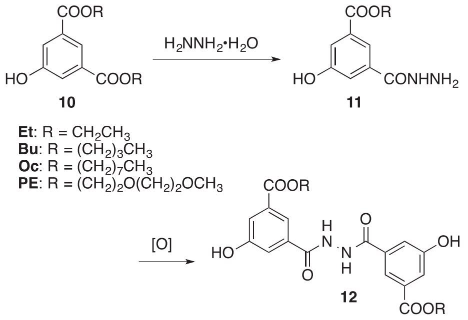
A small amount of the cured resin was placed between two flat specimens of the tested material, which were heated on a heating plate at 140 °C for 1 h. After cooling to room temperature, the bonded specimen was immersed in a 5% sodium hypochlorite solution.

2.16. Adhesion strength

The epoxy resin was heated with an equimolar amount of bisphenol at 80–130 °C to prepare a homogeneous mixture. After the addition of imidazole (10 mol%), the mixture was heated at 140 °C until it became homogenous. The mixture was spread between two aluminum plates (25 mm wide, 1.0 mm thick), and the adhesion area was set to 625 mm^2 (25 mm length). The plates were placed on a heating plate, with a weight of 1.2 kg placed on top. After heating at 140 °C for 3 h, the aluminum plates were cooled to room temperature to prepare single lap joint. The two plates were pulled from both sides to apply tensile-shear, and the maximum load at bond-breaking was measured for the calculation of adhesion strength.



Scheme 3.



Scheme 4.

3. Results and discussion

3.1. Design, synthesis, and solubility of bisphenols bearing diacylhydrazine moieties

Simple bisphenols bearing the diacylhydrazine moiety were prepared from phenolic carboxylic acid esters **1**, **4**, and **7,** as shown in Scheme 3. The above esters readily reacted with hydrazine hydrate to afford phenolic hydrazides **2**, **5**, and **8**, respectively. Oxidative coupling of these hydrazides with bis(acetyloxy)(phenyl)-λ^3-iodane [31] (PhI(OAc)$_2$) gave the corresponding diacylhydrazines **3**, **6**, and **9** in good yields.

The solubility of the prepared diacylhydrazines in epoxy resins was examined. Equimolar amounts of resins based on bisphenol A (**BPAER**) and butane-1,4-diol (**BDER**) were used (Chart 1). Both simple diacylhydrazines **3a** and **6** and methoxy-substituted diacylhydrazine **3b** were insoluble in all epoxy resins, even at high temperatures, which was rationalized by strong hydrogen bonding between diacylhydrazine moieties [32]. The flexible aliphatic diacylhydrazine **9** exhibited better solubility, dissolving in **BDER** above 80 °C, but still being insoluble in **BPAER**, even at high temperatures.

Ester groups were introduced onto the bisphenol scaffold to increase the solubility and prepare homogeneous mixtures with epoxy resins. To avoid steric hindrance, the positions *ortho* to the hydroxy group were left vacant. Furthermore, to avoid the formation of phthalazine [33], the ester moiety was introduced at the *meta* position of the hydrazide group. Thus, bisphenol **12** was rationally designed and synthesized from the corresponding diester **10** (Scheme 4). Ethyl (**10Et**), butyl (**10Bu**), octyl (**10Oc**), and 2-(2-methoxyethoxy)ethyl (**10PE**) esters were used. Hydrazination of **10** with 1 equiv of hydrazine monohydrate gave a mixture of **10**, **11**, and the corresponding bishydrazide, which can be removed from the reaction mixture due to its high solubility in water. Since the polarity of the hydrazide group is considerably higher than that of the ester group, **11** could be easily separated from **10**. Oxidative coupling of monohydrazide **11** was effectively carried out with Oxone® [34], except for **11PE**, because **12PE** was slightly soluble in water. For **11PE**, PhI(OAc)$_2$ was used as the oxidant, furnishing **12PE** in moderate yield. The structure of **12** was confirmed by a characteristic ^{1}H NMR signal of the phenolic OH group at 10.3 ppm and that of the diacylhydrazine NH group at 10.7 ppm.

The oxidation of diacylhydrazine **12** was examined. When **12** was treated with 5% sodium hypochlorite solution, rapid decomposition accompanied by the evolution of nitrogen gas was observed, resulting in a clear brown solution, which is indicative of phenol group oxidation.

The solubility of **12** in equimolar amounts of **BPAER** and **BDER** was examined. The ethyl and butyl esters, **12Et** and **12Bu**, respectively, did not form homogeneous mixtures even at 200 °C, although homogeneity could be achieved by the addition of a small amount of NMP. The amount of NMP required for the dissolution of **12Bu** was smaller than that for **12Et**. The octyl (**12Oc**) and polyether esters (**12PE**) formed homogeneous mixtures when heated. While a temperature of 120 °C was required for **12Oc**, **12PE** dissolved already at 40 °C. Thus, the solubility increased if an ester group with a long alkyl chain was introduced, and was further enhanced by the polyether functionality.

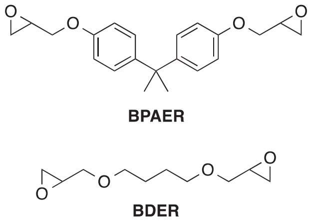


Chart 1.

3.2. Curing of epoxy resins and their properties

Curing was performed with 10 mol% of the imidazole catalyst added to the mixture of epoxy resin and bisphenol **12**, followed by heating to 130–140 °C. The curing temperature, the range for the exothermic reaction, was measured by DSC, with a heating rate of 5 °C/min. A small amount of NMP was added in the case of **12Et** and **12Bu** to make the mixture homogeneous. A typical DSC profile is shown in Fig. 1. The results are summarized in Table 1.

The curing temperature decreased slightly when an ester group with a long alkyl chain was introduced, the drop being even more pronounced when **12PE** was used as the curing agent. It seems that bisphenol solubility is responsible for these changes, with the curing inhibited by the aggregation of diacylhydrazine moieties due to strong hydrogen bonding. The aggregation effect is supposedly

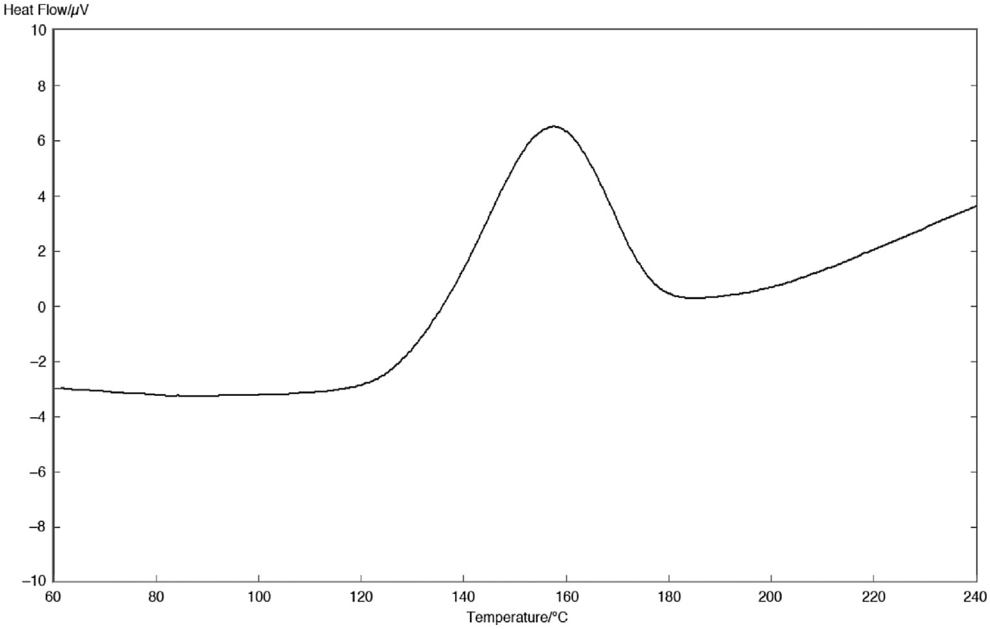


Fig. 1. DSC profile for the mixture of **12Et**, **BPAER**, 10 mol% of imidazole, and NMP at the heating rate of 5 °C/min.

less significant for the more soluble diacylhydrazines.

Oxidative degradation of the cured resin was investigated. When immersed in 5% sodium hypochlorite solution, every resin gradually decomposed with the evolution of nitrogen gas to give clear colorless solutions. Since brown color was not observed, the phenol groups in the curing agent were consumed during the curing process, and resin decomposition occurred by oxidative degradation of the diacylhydrazine moiety. The degradation rate could be roughly estimated from the rate of gas evolution. The epoxy resin cured by **12PE** decomposed most rapidly, and the one cured by bisphenol with a short alkyl ester moiety decomposed slower. The order of the decomposition rates was independent of the hydrophilicity of the curing agent, correlating with its solubility in the epoxy resin. Therefore, the dispersity of the diacylhydrazine moiety in the cured resin, rather than the attack of the hypochlorite anion and water, has a profound effect on the rate of decomposition.

Thermal stability of the cured resin was evaluated as the 5% weight loss temperature T_{d5} measured by TGA in air, with a heating rate of 10 °C/min. A typical TGA profile is shown in Fig. 2. The results are summarized in Table 2; the thermal stability of the epoxy resin cured by bisphenol A is also listed for comparison.

Since the epoxy resin cured with **12Et** exhibited a higher T_{d5} value than that cured with bisphenol A, the introduction of the diacylhydrazine moiety increased the thermal stability of the resin, probably due to its strong hydrogen bonding ability. However, the ester group with a long alkyl chain or the polyether chain decreased the thermal stability. In general, the epoxy resin cured by **12** shows comparable thermal stability to that of the resin cured by the nonfunctionalized bisphenol.

Table 1
Curing temperature of epoxy resin.[a]

Curing agent	Curing temperature (°C) for	
	BPAER	**BDER**
12Et	122–189	123–192
12Bu	129–191	129–195
12Oc	121–190	123–194
12PE	39–153	41–151

[a] **BPAER** or **BDER** was mixed with equimolar amount of **12** and 10 mol% of imidazole. The mixture was heated with monitoring heat flow by DSC (5 °C/min).

3.3. Adhesion and dismantling

Equimolar amounts of the epoxy resin and bisphenol **12** were mixed with 10 mol% of imidazole. For **12Et** and **12Bu**, a minimal amount of NMP was added, and the mixture was heated under stirring until homogenization. The resulting paste was placed between two flat materials, and the resin was cured at 140 °C for 1 h before the investigation of adhesive properties. The results are summarized in Table 3.

Glass was strongly and toughly bonded by all samples tested. Metal was also strongly and toughly bonded when **BPAER** was used. However, the adhesive became brittle when using **BDER**, with strong adhesion possible only when **12Et** was used as the curing agent. Natural rubber plates were not bonded with either epoxy resin. In the case of wood and paper, the resin infiltrated the material and did not work as an adhesive.

Adhesion strength was measured using aluminum plates and **BPAER**. To evaluate the intrinsic strength of the epoxy resin, **12Oc** and **12PE** were used as curing agents; the NMP component was unnecessary for these bisphenols. Bisphenol A was used as a reference curing agent. Two aluminum plates of 1 mm thickness were bonded with a homogeneous mixture of **BPAER**, bisphenol, and imidazole in a molar ratio of 1.0:1.0:0.1 to prepare single lap joint. A 1.2 kg weight was put on the plates, and the epoxy resin was cured at 140 °C for 3 h. The curing condition was not optimized. The plates were pulled from both sides to break the adhesive, with interfacial failure observed in every case. The tension was monitored by TMA to obtain the maximum load, which was divided by adhesion area to give adhesion strength [29,30]. The results are summarized in Table 4. The epoxy resin cured by **12** exhibited high adhesion strength, although it was reduced to 30–40% when diacylhydrazine moieties were introduced into bisphenol. The high crystallinity of the diacylhydrazine moiety makes the epoxy resin brittle, reducing the adhesive toughness.

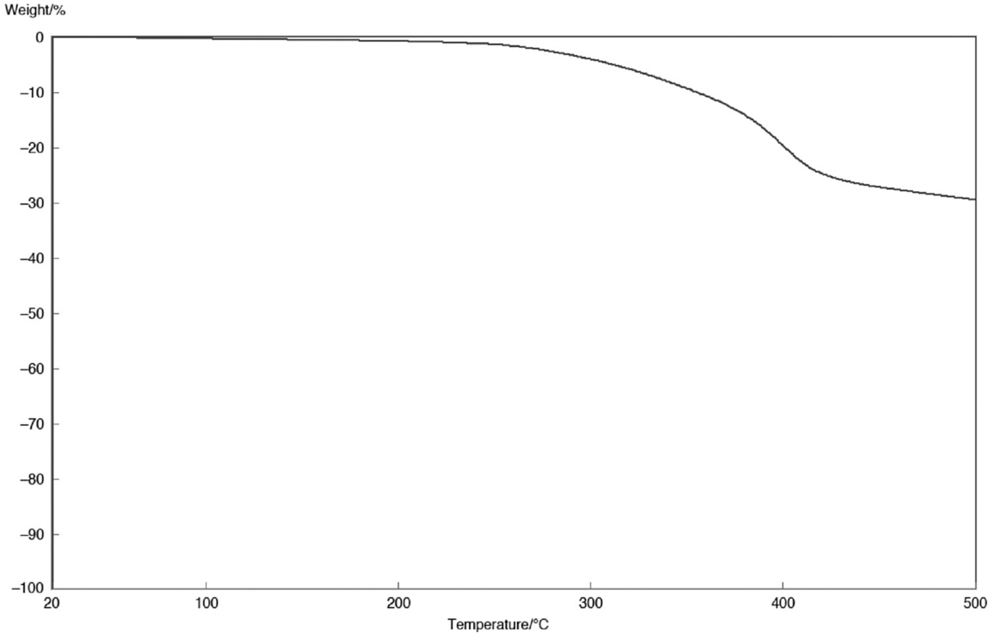


Fig. 2. TGA profile of **BPAER** cured by **12PE** and 10 mol% of imidazole at the heating rate of 10 °C/min in air.

Oxidative dismantling was investigated as follows. Two glass slide plates were bonded and placed in a sodium hypochlorite solution. Gas evolution started immediately, and the plates were spontaneously separated after a certain period. Even though the adhesive layer was very thin, the decomposition completed without any stirring, since the degradation products were small molecules. The mixing effect of the evolving nitrogen gas might help the infiltration of sodium hypochlorite solution into the space between the glass plates. The residual epoxy resin deposit remaining on glass finally disappeared after further treatment with sodium hypochlorite solution. The times for spontaneous dismantling are listed in Table 5.

Oxidative degradation of **BDER** was faster than that of **BPAER,** probably due to the more hydrophilic nature of **BDER**. The curing agent had a large effect on the rate of oxidative degradation: dismantling occurred faster when a more degradable resin was used as the adhesive.

4. Conclusion

Novel bisphenols bearing diacylhydrazine moieties were developed as curing agents for epoxy resins. Functionalizing the bisphenol with an ester group strongly enhanced its solubility, and homogeneous solvent-free mixtures were obtained for octyl and polyether esters. The epoxy resin cured by these bisphenols showed not only oxidative degradability by sodium hypochlorite solution, but also strong adhesion to glass and metal. The materials

Table 2
Thermal stability (T_{d5}) of cured epoxy resin.[a]

Curing agent	T_{d5} (°C)	
	BPAER	BDER
12Et	358	337
12Bu	312	318
12Oc	296	287
12PE	305	300
bisphenol A	322	–

[a] Measured by TGA (10 °C/min in air).

Table 3
The adhesive property of cured epoxy resin.[a]

Epoxy resin	Curing agent	Material				
		Glass	Metal[b]	Rubber	Wood	Paper
BPAER	**12Et**	T	T	N	N	N
BPAER	**12Bu**	T	T	N	N	N
BPAER	**12Oc**	T	T	N	N	N
BPAER	**12PE**	T	T	N	N	N
BDER	**12Et**	T	T	N	N	N
BDER	**12Bu**	T	B	N	N	N
BDER	**12Oc**	T	B	N	N	N
BDER	**12PE**	T	B	N	N	N

[a] T: tough, B: brittle, N: no adhesion.
[b] Aluminum, copper, and iron.

Table 4
Adhesion strength of cured resin for aluminum.[a]

Curing agent	Adhesive strength (MPa)
12Oc	1.5
12PE	1.1
bisphenol A	3.8

[a] **BPAER** is used as the epoxy resin. Two aluminum plates were adhered at 140 °C for 3 h with 1.2 kg of weight. The curing condition was not optimized.

Table 5
The period elapsed until the spontaneous debonding.[a]

Curing agent	Elapsed time (h)	
	BPAER	**BDER**
12Et	30	20
12Bu	30	20
12Oc	18	12
12PE	6	4

[a] Two slide glass plates were adhered by cured epoxy resin, and stood in sodium hypochlorite solution.

bonded by the cured resin were spontaneously oxidatively dismantled by treatment with sodium hypochlorite solution. The adhesion strength and oxidative degradability were dependent on the miscibility of the curing agent with the epoxy resin: while long alkyl and polyether chains increased both the curing agent miscibility and the degradability of the cured resin, these side chains also slightly decreased the thermal stability and adhesion strength of the cured resin. Among the bisphenols tested, **12Oc** turned out to be the most balanced curing agent for oxidatively degradable epoxy resins.

Supporting information

Supporting information, synthetic procedure for **2**–**9** and ^{1}H NMR, ^{13}C NMR, and IR spectra are available free of charge.

Acknowledgements

We thank the financial support of Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science (23550141) and MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2013–2017 (Creation of new fusion materials by integration of highly-ordered nano inorganic materials and ultra-precisely controlled organic polymers).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.06.066.

References

[1] J.M. Boyne, E.J. Millan, I. Webster, Peeling performance of a novel light switchable pressure-sensitive adhesive, Int. J. Adhes. Adhes. 21 (2001) 49–53.
[2] E.M. White, J.E. Seppala, P.M. Rushworth, B.W. Ritchie, S. Sharma, J. Locklin, Switching the adhesive state of catecholic hydrogels using phototitration, Macromolecules 46 (2013) 8882–8887.
[3] K. Ebe, H. Seno, K. Horigome, Uv curable pressure-sensitive adhesives for fabricating semiconductors. I. Development of easily peelable dicing tapes, J. Appl. Polym. Sci. 90 (2003) 436–441.
[4] S.R. Trenor, T.E. Long, B.J. Love, Development of a light-deactivatable PSA *via* photodimerization, J. Adhes. 81 (2005) 213–229.
[5] T.-Z. Wang, L. Li, F.-S. Du, Z.-C. Li, A facile approach to catechol containing UV dismantlable adhesives, Polymer 68 (2015) 270–278.
[6] K. Ogino, J.-S. Chen, C.K. Ober, Synthesis and characterization of thermally degradable polymer networks, Chem. Mater 10 (1998) 3833–3838.
[7] L. Wang, H. Li, C.P. Wong, Syntheses and characterizations of thermally reworkable epoxy resins II, J. Polym. Sci. Part A Polym. Chem. 38 (2000) 3771–3782.
[8] J.R. Mcelhanon, E.M. Russick, D.R. Wheeler, D.A. Loy, J.H. Aubert, Removable foams based on an epoxy resin incorporating reversible diels-alder adducts, J. Appl. Polym. Sci. 85 (2002) 1496–1502.
[9] E. Sato, H. Tamura, A. Matsumoto, Cohesive force change induced by polyperoxide degradation for application to dismantlable adhesion, ACS Appl. Mater. Interfaces 2 (2010) 2594–2601.
[10] E. Sato, T. Hagihara, A. Matsumoto, Facile synthesis of main-chain degradable block copolymers for performance enhanced dismantlable adhesion, ACS Appl. Mater. Interfaces 4 (2012) 2057–2064.
[11] M. Sugimoto, M. Yamamoto, Development of dismantlable adhesives which utilized the decomposition acceleration effect of oxidizer, Sci. Technol. Energy Mater 73 (2012) 63–69.
[12] T. Higashihara, M.-C. Fu, T. Uno, M. Ueda, Synthesis and characterization of polycyanurates as dismantlable adhesives, J. Polym. Sci. Part A Polym. Chem. 54 (2016) 1153–1158.
[13] Y. Nishiyama, N. Uto, C. Sato, H. Sakurai, Dismantlement behavior and strength of dismantlable adhesive including thermally expansive particles, Int. J. Adhes. Adhes. 23 (2003) 377–382.
[14] H. Ishikawa, K. Seto, S. Shimotuma, N. Kishi, C. Sato, Bond strength and disbonding behavior of elastomer and emulsion-type dismantlable adhesives used for building materials, Int. J. Adhes. Adhes. 25 (2005) 193–199.
[15] T. Inui, E. Sato, A. Matsumoto, Pressure-sensitive adhesion system using acrylate block copolymers in response to photoirradiation and postbaking as the dual external stimuli for on-demand dismantling, ACS Appl. Mater. Interfaces 4 (2012) 2124–2132.
[16] T. Inui, K. Yamanishi, E. Sato, A. Matsumoto, Organotellurium-mediated living radical polymerization (TERP) of acrylates using ditelluride compounds and binary azo initiators for the synthesis of high-performance adhesive block copolymers for on-demand dismantlable adhesion, Macromolecules 46 (2013) 8111–8120.
[17] K. Yamanishi, E. Sato, A. Matsumoto, Precise synthesis of acrylic block copolymers and application to on-demand dismantlable adhesion systems in response to photoirradiation and postbaking, J. Photopolym. Sci. Technol. 26 (2013) 239–244.
[18] T. Inui, E. Sato, A. Matsumoto, High-molecular-weight polar acrylate block copolymers as high-performance dismatlable adhesive materials in response to photoirradiation and postbaking, RSC Adv. 4 (2014) 24719–24728.
[19] E. Sato, K. Taniguchi, T. Inui, K. Yamanishi, H. Horibe, A. Matsumoto, Dismantling behavior of pressure sensitive adhesives using acrylic block and random copolymers in response to photoirradiation and postbaking, J. Photopolym. Sci. Technol. 27 (2014) 531–534.
[20] E. Sato, K. Yamanishi, T. Inui, H. Horibe, A. Matsumoto, Acetal-protected acrylic copolymers for dismantlable adhesives with spontaneous and complete removability, Polymer 64 (2015) 260–267.
[21] S. Leijonmarck, A. Cornell, C.-O. Danielsson, G. Lindbergh, Electrochemical characterization of electrically induced adhesive debonding, J. Electrochem. Soc. 158 (2011) 109–114.
[22] S. Leijonmarck, A. Cornell, C.-O. Danielsson, T. Akermark, B.D. Brandner, G. Lindbergh, Electrolytically assisted debonding of adhesives: an experimental investigation, Int. J. Adhes. Adhes. 32 (2012) 39–45.
[23] M. Kobayashi, M. Terada, A. Takahara, Reversible adhesive-free nanoscale adhesion utilizing oppositely charged polyelectrolyte brushes, Soft Matter 7 (2011) 5717–5722.
[24] M. Kobayashi, A. Takahara, Environmentally friendly repeatable adhesion using a sulfobetaine-type polyzwitterion brush, Polym. Chem. 4 (2013) 4987–4992.
[25] N. Kihara, R. Ii, A. Ogawa, Synthesis and properties of nylon-0,2–oxidatively degradable polymer that is stable in air, J. Polym. Sci. Part A Polym. Chem. 45 (2007) 963–967.
[26] N. Kihara, Y. Iino, T. Misawa, Oxidative degradation of poly(-isophthaloylhydrazine-1,2-diyl)s, J. Polym. Sci. Part A Polym. Chem. 46 (2008) 6255–6262.
[27] K. Nagashima, N. Kihara, Y. Iino, Oxidative coupling polymerization of bishydrazide for the synthesis of poly(diacylhydrazine): oxidative preparation of oxidatively degradable polymer, J. Polym. Sci. Part A Polym. Chem. 50 (2012) 4230–4238.
[28] K. Nagashima, N. Kihara, Oxidation driven crosslinking-decrosslinking of polymer and its application for recyclin, Kobunshi Ronbunshu 70 (2013) 704–711.
[29] S.J. Shaw, Epoxy resin adhesives, in: B. Ellis (Ed.), Chemistry and Technology of Epoxy Resins, Chapman & Hall, London, 1993, pp. 206–255.
[30] T.M. Goulding, Epoxy resin adhesives, in: A. Pizzi, K.L. Mittal (Eds.), Handbook of Adhesive Technology, second ed., Marcel Dekker, New York, 2003, pp. 823–838 revised and expanded.
[31] O. Prakash, V. Sharma, A. Sadana, Hypervalent iodine oxidation of acid hydrazides: a new synthesis of *N*,*N*'-Diacylhydrazines, Synth. Commun. 27 (1997) 3371–3377.
[32] Y. Ohsedo, M. Muyamoto, H. Watanabe, M. Oono, A. Tanaka, Alkylhydrazide derivatives as new organogelators and their potential ability to gel electrolytes, Bull. Chem. Soc. Jpn. 86 (2013) 671–673.
[33] Th Curtius, E. Davis, Hydrazides and azides (azoimides) of the phthalic acids, J. Prakt. Chem. 54 (1896) 66–87.
[34] P.P. Kulkarni, A.J. Kadam, U.V. Desai, R.B. Mane, P.P. Wadgaonkar, A simple and efficient oxidation of hydrazides to *N*,*N*'-Diacylhydrazines using Oxone in an aqueous medium, J. Chem. Res. S (2000) 184–185.