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

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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

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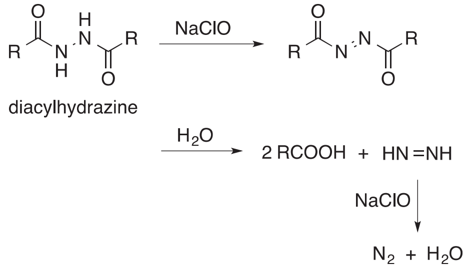


Scheme 1.

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.

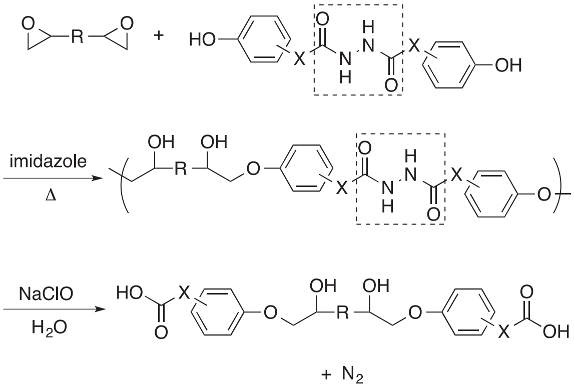
2.2. 10Et

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.