

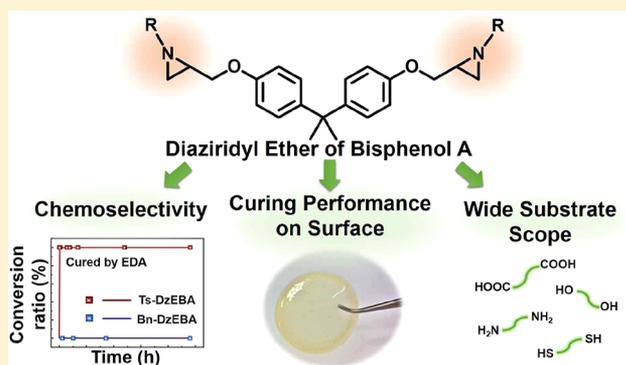
Diaziridyl Ether of Bisphenol A

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Supporting Information

ABSTRACT: Increased complexities in applications involving curable materials virtually need new materials that can overcome the limitations of existing ones. Resins, the structure of which is based on bisphenol A backbone terminated with three membered N-heterocycles—aziridines—have been synthesized, and their thermal-curing performance in solution and solid state was evaluated by NMR and FT-IR spectroscopies, differential scanning calorimetry, and single lap shear strength test and compared with that of analogous epoxy resin (diglycidyl ether of bisphenol A; DGEBA). Results reveal that the chemical reactivity of the aziridine-based resins is fine-tunable by controlling the *N*-substituent of aziridine. These resins can undergo ring-opening polymerization in the presence of various curing agents under unprecedentedly mild conditions and show remarkably rapid curing rate, wide substrate scope, and excellent chemoselectivity as compared to the analogous epoxy resin. Our results demonstrate superb curing ability of aziridine, making it promising for applications in materials and polymer sciences.



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INTRODUCTION

The field of curable materials is highly multidisciplinary and competitive given a wide range of applications ranging from surface modification¹ and adhesive² to dielectric films³ and nanomaterials.⁴ From a chemistry perspective, epoxy is arguably one of the successful curable materials and has been the focus of the majority of research in the field.^{5–7} Figure 1a summarizes some examples for utility of epoxy.^{8–11} Epoxy materials, however, do face certain limitations, and intense research is taking place to develop new curable materials with improved properties.^{12,13} In recent years, structurally modified epoxy resins have been developed to enhance curing rate,¹⁴ reduce reaction temperature,¹⁵ and improve chemoselectivity¹⁶ and substrate scope.¹⁷ All of these properties are desirable for resolving the challenges in epoxy-related materials, and although these studies are early and limited in number, they highlight the opportunities that arise when the chemical structure of epoxide, a core functional group in epoxy, is further modified.

Many problematic features in epoxy materials rely on intrinsic chemical properties of epoxide. Engineering chemical properties of epoxide is limited because of divalent bonding nature of oxygen. A neighbor compound of epoxide, aziridine (Figure 1b)—three-membered N-heterocycle—should prove even more useful for improving and tailoring chemical properties of curable materials and perhaps leads to curing ability that cannot be achieved by epoxy. Specifically, aziridine is based on trivalent nitrogen and can offer a unique opportunity to tune the chemical property through rational design of the *N*-substituent.^{18–21} For example, aziridine possessing an electron-withdrawing group (EWG) such as

tosyl and mesyl for the *N*-substituent undergoes ring-opening reaction under basic conditions.^{22,23} On the other hand, ring-opening reaction of aziridine with an electron-donating group (EDG) such as the alkyl moiety for *N*-substituent barely proceeds until it is activated by a Lewis acid.^{24,25} Aziridines have been utilized mainly for synthesis of small molecules with complex structures through regio-^{26,27} and enantioselective^{28,29} ring-opening reaction of aziridine, and click chemistry was achieved by conjugate reaction of aziridine.^{30,31} A limited number of literatures have also reported ring-opening polymerization (ROP) of aziridine monomers, and these often relied on *N*-EWG-aziridine derivatives.^{32–34} Despite a fairly long history of aziridine in organic synthesis, the ability of aziridine for curable materials has been rarely established.

Although there are a few aziridine-based cross-linkers available in the market (see the Supporting Information for their structures), they are often limited to carboxylic acid substrates,³⁵ and rather surprisingly, little has been investigated regarding whether aziridine can indeed offer the ability as curing resin for surpassing conventional epoxy. In this work, we wish to provide detailed information on properties of aziridine-based thermal cure resins in a chemistry point of view and thereby gauge the potential of aziridine for the development of resin by replacing epoxide in a prevalent epoxy material with aziridine and comparing each other in the context of curing performance. A representative epoxy resin in polymer industry and materials science is diglycidyl ether of bisphenol A

Received: March 14, 2018

Revised: May 11, 2018

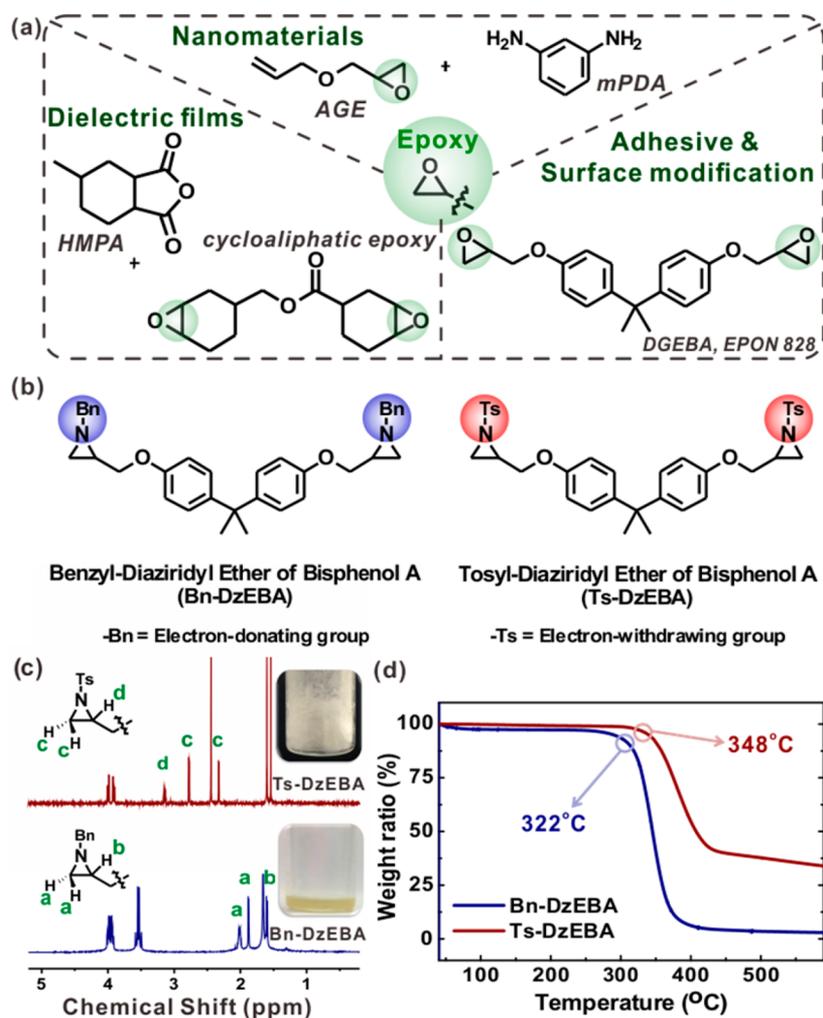


Figure 1. (a) Examples of epoxy resins for curable materials where epoxide plays a key role in curing performance (AGE: allyl glycidyl ether; *m*PDA: *m*-phenylenediamine; DGEBA: diglycidyl ether of bisphenol A; HMPA: hexahydro-4-methylphthalic anhydride). (b) Two types of diaziridyl ether of bisphenol A (denoted as DzEBA) and Ts-DzEBA including EDG and EWG substituents, respectively, at the nitrogen of aziridine. These are the analogues of diglycidyl ether of bisphenol A (DGEBA). (c) ¹H NMR spectra of Ts- and Bn-DzEBAs. Insets are photos of purified and dried DzEBAs. (d) Traces of thermogravimetric analysis (TGA).

(DGEBA; Figure 1a) containing the backbone of bisphenol A, which is inexpensive and easily accessible as well as mechanical-strengthening- and thermal-resistant.^{36–39} If one could create analogous curing resins with unexplored or new functional moiety over the same backbone, one could straightforwardly compare their curing performances to unveil the potential of the tested moiety for a new class of curing resin. Herein we describe synthesis of aziridine-based curing resins, diaziridyl ether of bisphenol A (denoted as DzEBA; Figure 1b), and a study that determines their performance for thermal curing, which underlies ROP of two terminal aziridines. Analysis of the thermal-curing process of DzEBA resins over various curing agents with NMR and FT-IR spectroscopies, differential scanning calorimetry (DSC), and single lap shear strength test in solution or solid state indicates that the curing ability of DzEBAs largely depends on the electronic structure of the *N*-substituent of aziridine, proceeds unprecedentedly fast under mild conditions, and exhibits excellent chemoselectivity and wide substrate scope. These attractive features provide molecular insight into the potential utility of aziridines for developing novel curing resins and for overcoming the limitations of conventional epoxy. Furthermore, we envision

that the chemoselectivity of resins demonstrated here would bring benefit to the design of heterogeneous resin scaffold for advanced polymeric systems.⁴⁰

RESULTS AND DISCUSSION

We prepared DzEBAs having *N*-Bn and *-Ts* as *N*-EDG and *-EWG* aziridines, respectively; the Supporting Information contains detailed synthetic procedures and characterization data for them. Briefly, Bn-DzEBA was synthesized by coupling reaction between bisphenol A and *N*-benzylaziridine having methyl tosylate at the C-2. For Ts-DzEBA, DGEBA was ring-opened with *p*-toluenesulfonamide followed by mesylation and ring-closure reactions. All analytical data, including ¹H and ¹³C NMR spectroscopies, and electrospray ionization mass spectrometry (ESI-MS) were in full agreement with the proposed structures. For example, the ¹H NMR spectra of DzEBAs in Figure 1c exhibit highly diagnostic resonances at 2.78 ($J_{\text{H-H}} = 7$ Hz) and 2.33 ppm ($J_{\text{H-H}} = 4.6$ Hz) as doublets for Ts-DzEBA and at 1.88 ppm ($J_{\text{H-H}} = 3.5$ Hz) and 1.61 ppm ($J_{\text{H-H}} = 6.7$ Hz) as doublets for Bn-DzEBA, indicative of the two inequivalent hydrogen atoms in the aziridine rings. The carbons at C-2 for the aziridines in Bn- and Ts-DzEBAs were

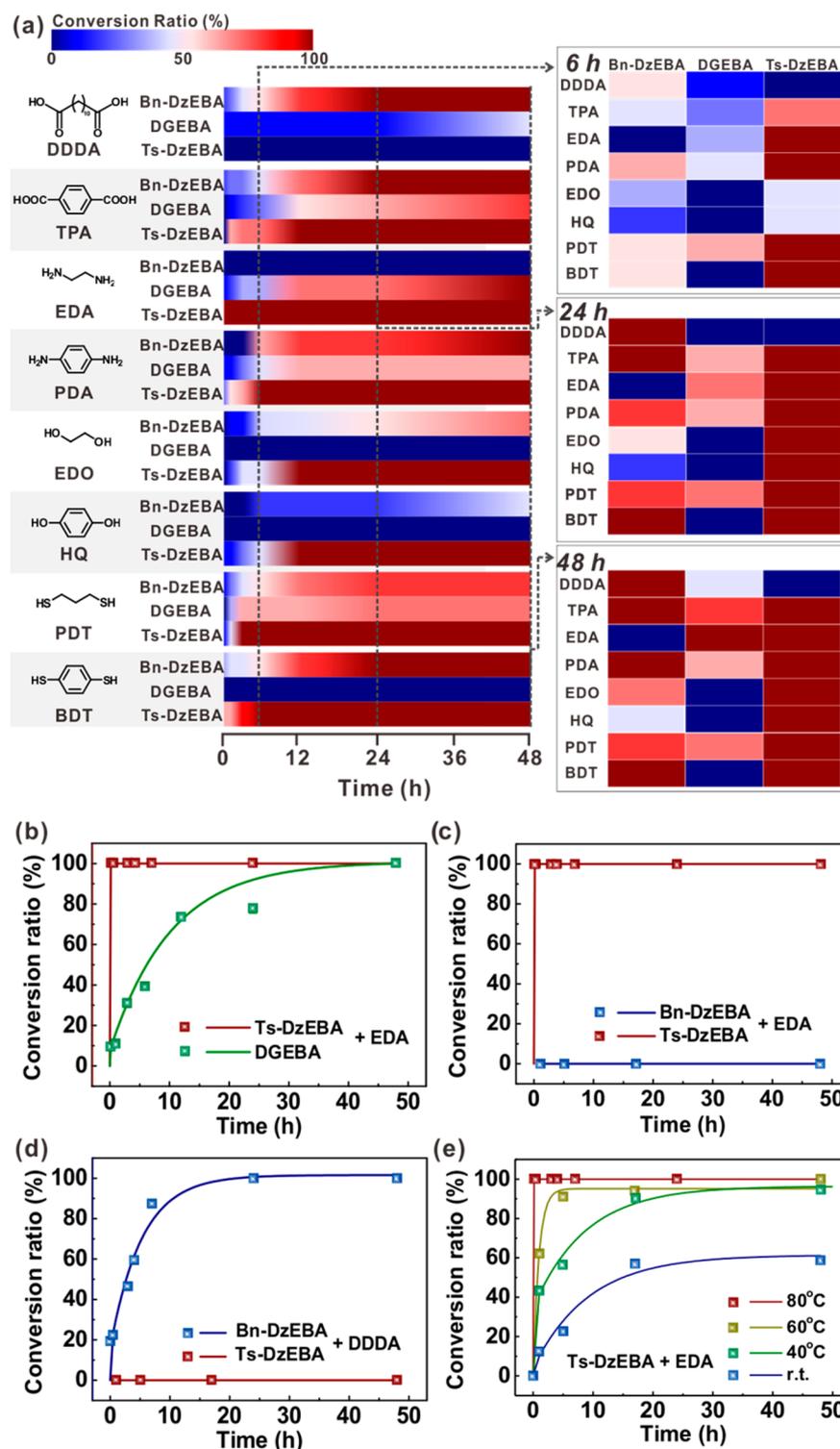


Figure 2. (a) 2D heatmaps of conversion ratio for ROP of DzEBAs and DGEBA resins in the presence of various curing agents at 80 °C monitored by ^1H NMR spectroscopy. Heatmaps for 6, 24, and 48 h are exemplary plots to show chemoselectivity at different reaction times. Curing agents used for ROP test were dodecanedioic acid (DDDA), terephthalic acid (TPA), ethylenediamine (EDA), *p*-phenylenediamine (PDA), ethylenediol (EDO), hydroquinone (HQ), 1,3-propanedithiol (PDT), and 1,4-benzenedithiol (BDT). (b) Comparison of reaction kinetics for Ts-DzEBA and DGEBA in the presence of ethylenediamine (EDA). (c) Chemoselectivity for the DzEBAs over a curing agent, EDA. (d) Chemoselectivity for DzEBAs over a curing agent, alkyl diacid (dodecanedioic acid; DDDA). (e) Dependence of ROP of Ts-DzEBA by EDA on reaction temperature.

stereocenters. For the stereochemistry of products, thin layer chromatography (TLC) monitoring during synthesis showed new single spot indicating one product, and ^1H NMR spectra also showed the presence of one type of aziridine. To

determine the number of stereoisomers, we conducted chiral HPLC analysis and found that there were three peaks with 1:2:1 integration ratio for the products. This finding could be attributed to the presence of two meso compounds and two

diastereomers. See the [Supporting Information](#) for detailed chiral HPLC data and the stereoisomer structures. The thermal and optical properties of DzEBAs were investigated. [Figure 1d](#) shows the thermogravimetric analysis (TGA) profile over the temperature range from 30 to 600 °C for the DzEBAs. Thermal degradation beginning at ~322 and ~348 °C for Bn-DzEBA and Ts-DzEBA, respectively, was observed. For comparison, DGEBA begins to decompose thermally at ~370 °C.⁴¹ Ts- and Bn-DzEBAs were white powder and light-yellowish viscous liquids in ambient condition, respectively (the insets in [Figure 1c](#); see the [Supporting Information](#) for UV-vis absorption spectra).

To determine the substrate scope and chemoselectivity for the ROP of DzEBAs, compared to that of DGEBA as a control, we carried out ¹H NMR spectroscopic analysis for ROP over various curing agents (structurally simple alkyl/aryl amines, acids, alcohols, and thiols) in solution under identical reaction conditions (80 °C in DMSO-*d*₆ containing 1:1 mole ratio of resin (Ts-DzEBA, Bn-DzEBA, or DGEBA) and curing agent, in air; see the [Supporting Information](#) for details). For investigating curing performance, we set the temperature of 80 °C as the highest; in preliminary experiments, we have surveyed the performance of thermal curing of DzEBAs over a wide range of temperature and found that the curing for the Ts-DzEBA and ethylenediamine combination was completed in few minutes at 80 °C. This temperature was sufficient to determine whether DzEBAs function under mild conditions as compared to DGEBA. [Figure 2](#) shows chemical structures of curing agents we tested and summarizes the results. We observed four significant features. (i) Overall, DzEBAs showed a pronouncedly wide substrate scope: alkyl and aryl acids, alcohols, amines, and thiols acted as efficient curing agents. However, the ROP of DGEBA was triggered limitedly by amines, aryl acid, and alkyl thiol; DGEBA remained completely intact or showed very sluggish reaction over alkyl acid, alkyl/aryl alcohols, and aryl thiol ([Figure 2a](#)). (ii) The ROP for DzEBAs proceeded remarkably rapidly under mild conditions as compared to that of DGEBA. For example, the ROP of Ts-DzEBA in the presence of alkylamine (ethylenediamine; EDA) was completed within 10 min at 80 °C; the analogous reaction with DGEBA showed ~10% conversion (the ratio of product to the initial reactant, determined by ¹H NMR analysis) in 10 min under the identical condition. ([Figure 2b](#)). (iii) The ROP of DzEBAs exhibited excellent chemoselectivity: alkyl acid (dodecanedioic acid; DDDA) was relevant to Bn-DzEBA and not Ts-DzEBA, whereas alkylamine (EDA) chemoselectively opened only Ts-DzEBA ([Figure 2c,d](#)). These findings led to the conclusion that, unlike DGEBA, the curing performance of DzEBAs is highly efficient and chemoselective over different curing agents. The chemoselectivity of DzEBAs was attributed to the controlled electronic structure on the *N*-substituent in aziridine.^{19,42}

We further investigated the dependence of rate of DzEBAs' ROP on reaction temperature. [Figure 2e](#) shows exemplary plots of conversion ratio for a mixture of Ts-DzEBA and EDA at variable temperatures. The rate of ROP increased as the temperature increased from 25 to 80 °C; rather surprisingly, the reaction was completed in 10 min at 80 °C whereas the analogous reaction of DGEBA proceeded slowly in the same reaction time. The ROP reaction of Ts-DzEBA was completed even at 40 °C. Bn-DzEBA exhibited the similar correlation with reaction temperature: as shown in [Figure S26](#) of the [Supporting Information](#), the rate of Bn-DzEBA's ROP increased as the

temperature increased from 25 to 80 °C, and also the ROP was completed even at 40 °C.

We conducted DSC studies to investigate the cure process of resin-curing agent formulations under solvent-free conditions in a nonisothermal manner.^{43–45} For nonisothermal DSC study, samples containing 1:1 mole ratio of individual resins and curing agents (shown in [Figure 2a](#)) were cured at various heating rates from 2 to 20 °C/min. Note that some of curing and unsuitable for DSC experiment; hence, the alkylamine and alcohol were replaced with 1,12-diaminododecane (DAD) and 1,12-dodecanediol (DDD) (shown in [Table S1](#)). Alkyl thiol suitable to DSC study was not accessible. Under the same curing condition, the peak temperature (T_p) was measured and taken as an indicator to compare the reactivity of curing process for various formulations.⁴⁶

Some of results of DSC experiments are summarized in [Table 1](#) (see the [Supporting Information](#) for the other data).

Table 1. Curing Characteristics of Various Resin-Curing Agent Formulations at 20 K/min^a

curing agent	curing resin	T_p [°C]	E_a^b [kJ/mol]	ΔH [J/g]
PDA	DGEBA	135	78	386
PDA	Ts-DzEBA	96	113	20
DDDA	Bn-DzEBA	113	121	21
DAD	DGEBA	133	58	425
DAD	Ts-DzEBA	76 ^c	– ^c	– ^c

^aOut of 21 resin-curing agent formulations, five formulations showed single exothermic peaks corresponding to thermal curing. ^bValues of E_a were determined with DSC curves measured at different heating rates and [eq 1](#). ^cAn exothermic peak was overlapped with the melting point of DAD, and we were unable to estimate meaningful values of E_a and ΔH .

Out of 21 formulations, seven (PDA/DGEBA, PDA/Ts-DzEBA, DDDA/Bn-DzEBA, DAD/DGEBA, DAD/Ts-DzEBA, BDT/Bn-DzEBA, and BDT/Ts-DzEBA) were relevant to DSC studies. The rest of formulations did not show peaks corresponding to the curing process; only endothermic peaks corresponding to melting process of resins and curing agents were observed (see the [Supporting Information](#) for DSC curves). Results in DSC experiments could be summarized as follows. (i) Each of the formulations relevant to DSC exhibited single exothermic peaks, indicative of thermal curing. (ii) The tested formulations showed that T_p increased with increasing heating rate (see exemplary plots in [Figure 3a–d](#)). (iii) Overall, the DzEBAs showed lower T_p values than DGEBA. For example, T_p (~96 °C) for Ts-DzEBA/PDA was lower than the analogous system of DGEBA (~135 °C) ([Table 1](#)).

While DGEBA was not cured by DDDA, the Bn-DzEBA/DDDA system showed T_p of ~113 °C ([Figure 3c](#)). (iv) Chemoselectivity was observed: PDA was relevant to Ts-DzEBA and not Bn-DzEBA. On the other hand, Bn-DzEBA, not Ts-DzEBA, was cured well by DDDA. The excellent curing performance and chemoselectivity of DzEBAs were consistent with the results of ¹H NMR study shown in [Figure 2](#). (v) Thermal curing of Ts-DzEBA in the presence of DAD was much faster than that of DGEBA ([Figure 3d,e](#)), and the exothermic peak of curing appeared at the low-temperature region where the endothermic peak corresponding to the melting point of DAD (67–69 °C) appeared. Although estimating T_p for this system was not accurate, it was no doubt that the thermal curing was remarkably rapid.

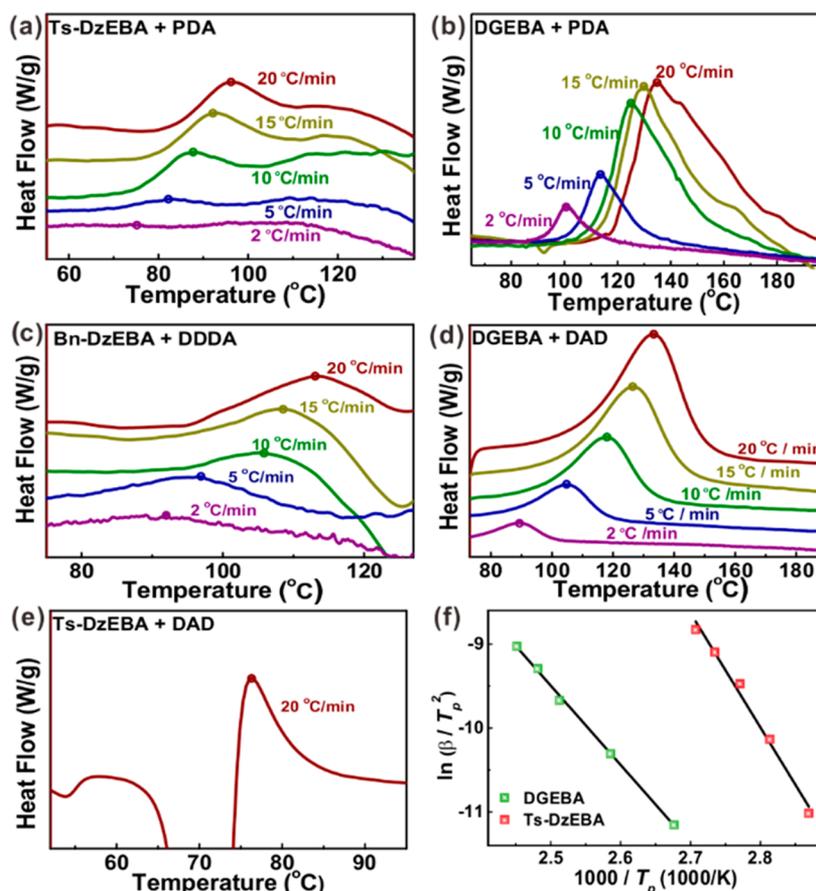


Figure 3. DSC thermograms of (a) Ts-DzEBA/*p*-phenylenediamine (PDA), (b) DGEBA/PDA, (c) Bn-DzEBA/dodecanedioic acid (DDDA), (d) DGEBA/1,12-diaminododecane (DAD), and (e) Ts-DzEBA/DAD at different heating rates (2, 5, 10, 15, and 20 °C/min). (f) Linear plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for two resins (DGEBA and Ts-DzEBA) cured by PDA based on Kissinger's equation (eq 1). Circles in the plots indicate peak temperature (T_p).

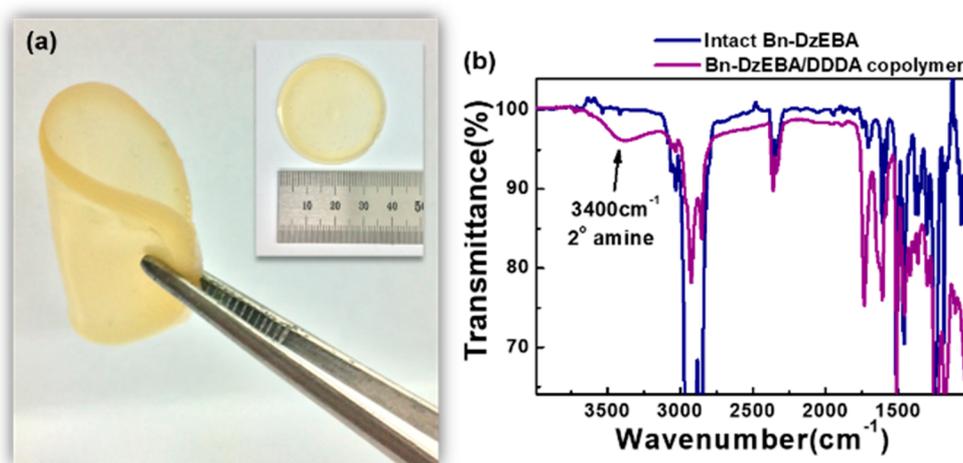


Figure 4. Cured film of Bn-DzEBA/DDDA formed by a conventional solvent-cast method. (a) Photos of the film after thermal curing at 80 °C for 3 h. (b) ATR FT-IR spectra of the film and intact Bn-DzEBA resin.

The DSC curves of DzEBAs cured with aryl acid (terephthalic acid; TPA) and aryl alcohol (hydroquinone; HQ) did not display exothermic peak, indicating no cure occurred (Figures S29 and S31). This finding was inconsistent with that of ^1H NMR study and could be explained with the high melting point of TPA (mp = 300 °C) and HQ (mp = 172 °C). These curing agents were not melt in the temperature

range we examined and thus did not mix with curing resins for DSC experiments.

According to Kissinger's method,⁴³ the activation energy (E_a) for curing process could be estimated in nonisothermal DSC study using eq 1. Here, T_p is the peak temperature, β is heating rate, A is pre-exponential factor, and R is the universal gas constant.

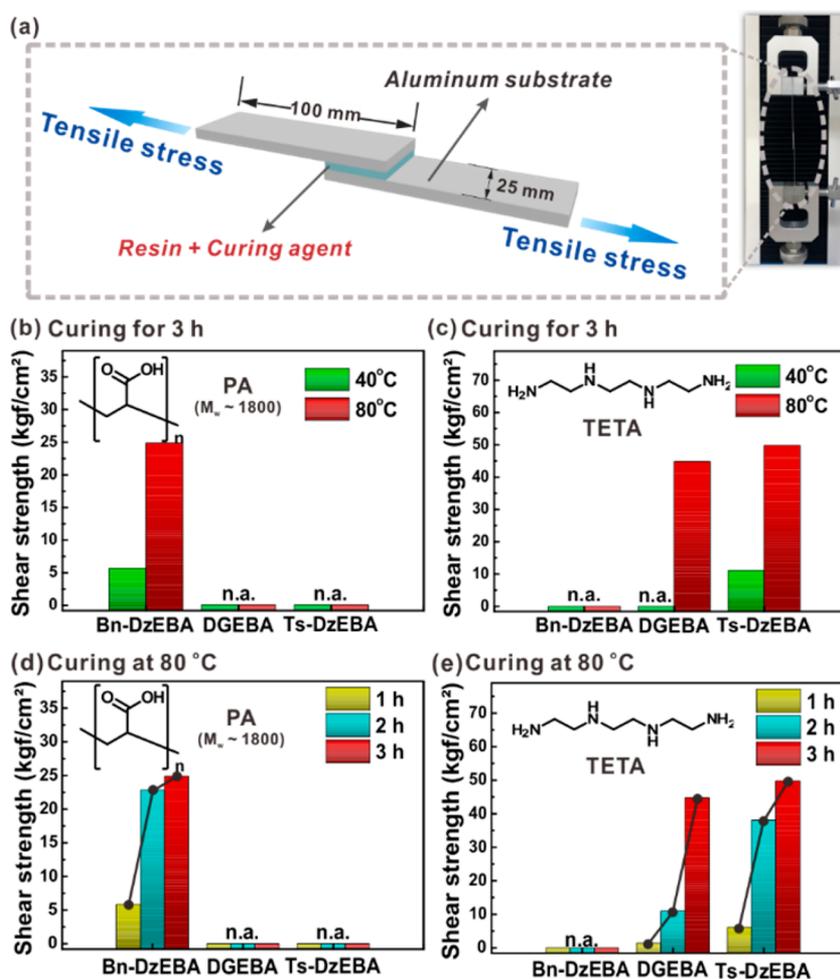


Figure 5. (a) Scheme of the single lap shear test and the lap shear strength. Shear strength measured (b, c) at different curing temperatures and (d, e) different curing times. PA and TETA are poly(acrylic acid) and triethylenetetramine, respectively, as curing agent (n.a. = no adhesion).

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (1)$$

Figure 3f shows the plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for DGEBA and Ts-DzEBA cured by PDA, and the slope of linear fitting plots corresponds to $-E_a/R$. The E_a value (~ 78 kJ/mol) of the DGEBA/PDA system is lower than that (~ 113 kJ/mol) of Ts-DzEBA/PDA. This difference in E_a was attributed to the different nature of ROP for aziridine and epoxide.⁴⁷ This was also reflected into the difference in ΔH : as shown in Table 1, there was approximately 1 order of magnitude difference in ΔH between DzEBAs and DGEBA.

According to Arrhenius equation ($k = A \exp(-E_a/RT)$ where k is the rate constant, A is the pre-exponential factor, R is the universal gas constant, and T is the reaction temperature), the rate constant k is associated with not only activation energy E_a but also pre-exponential factor A which is intrinsic to chemical reaction. In Kissinger's method, we were able to estimate the A factor: $\log(A)$ values for thermal curing of Ts-DzEBA and DGEBA with PDA were ~ 13.4 and ~ 7.1 , respectively. While the difference in E_a for Ts-DzEBA and DGEBA was little ($\times \sim 1.5$), the difference in A was significant ($\times \sim 10^6$). The Arrhenius equation led us to estimate the k values over the temperature range (from ~ 300 to ~ 500 K) tested in this work: at 300 K, the k values for Ts-DzEBA/PDA and DGEBA/PDA

were similar ($\Delta k = \sim 2 \times 10^{-4} \text{ s}^{-1}$), and at 500 K the k value of Ts-DzEBA/PDA was ~ 400 times larger than that of DGEBA/PDA. Overall, these findings indicate the curing rate for DzEBA is dominated by the A factor rather than the E_a , which accounts for the great curing performance of DzEBAs as compared to DGEBA.

The feasibility of DzEBAs as curing resin in solid state was further demonstrated by thermally curing a millimeter thick film comprising resin and curing agent. A film of *N*-Bn-DzEBA and DDDA mixture at 1:1 molar ratio was formed through a simple solvent-cast process (see the Supporting Information for details). Upon thermal curing at 80 °C for 3 h the liquid film was converted into the corresponding solid form (Figure 4a). The completion of ROP could be determined by ATR FT-IR spectroscopic analysis (Figure 4b): comparison of FT-IR spectra before and after thermal curing exhibited the appearance of new transmittance peak at $\sim 3400 \text{ cm}^{-1}$, which corresponded to secondary amine and confirmed the formation of the desired ring-opened product.

One of applications for epoxy materials is to adhere materials together via surface bonding.^{48,49} Thus, we further compared the adhesion performance for the resins through single lap shear strength test based on ASTM D3163 (Figure 5a). We used poly(acrylic acid) (PA)⁵⁰ and triethylenetetramine (TETA)⁵¹ as curing agents; these have been previously tested for DGEBA resin. In a typical experiment, a 1:1 mixture of resin

(0.11 M; Ts- or Bn-DzEBA, or DGEBA) and curing agent (0.11 M) in THF was homogeneously placed by spin-coating between prerinced aluminum substrates, and shear strength was measured by a universal testing machine (UTM). Figure 5b,c shows the results. Overall, the adhesives including DzEBAs (~25 and ~50 kgf/cm² for Bn-DzEBA/PA and Ts-DzEBA/TETA) showed higher shear strength than those including DGEBA (0 and ~44 kgf/cm²). DzEBAs displayed adhesion performance when curing temperature was lowered from 80 to 40 °C. As other experiments above, chemoselectivity was observed for DzEBAs. The use of PA resulted in adhesion for only Bn-DzEBA while TETA was relevant to Ts-DzEBA and not Bn-DGEBA. In the plots of shear strength as a function of curing time (Figure 5d,e) we were able to confirm that DzEBAs were cured rapidly as compared to DGEBA.

CONCLUSIONS

In conclusion, the experiments reported in this work were designed particularly to compare systematically the performance of aziridine-containing curing resins with the analogous epoxy-based curing resin. We replaced the epoxide terminal units in DGEBA with the *N*-EDG or -EWG aziridines while keeping other structures and reaction conditions constant and found that the chemistry of aziridines could be exploited for achieving efficient curing resin and overcoming critical limitations observed in epoxy-based resin: sluggish curing rate, harsh reaction conditions, narrow substrate scope, and no or little chemoselectivity. Although it should be further improved for satisfying industrial needs such as cost-effectiveness and large-scale synthesis, this work demonstrates, as a proof-of-concept, the utility of aziridines as a new functional moiety for curing resin.

EXPERIMENTAL SECTION

Materials. All reagents were used as supplied unless otherwise specified. All organic solvents were purchased from Daejung while water was purified using an Aqua MAX-Basic System (deionized water, electrical resistivity of which is ~18.2 MΩ·cm).

Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker FT-NMR Advance-500 using CDCl₃ and DMSO as solvent and residual solvents as an internal standard. Chemical shifts are expressed in parts per million (ppm) related to internal TMS, and coupling constants (*J*) are in hertz. MS (ESI-QTOF) measurements were recorded on a Bruker compaq Q-TOF MS. UV-vis spectra were measured using Agilent Technologies 8453 UV-vis spectrometer. Measurements of FT-IR were carried out using a Bruker ALPHA FT-IR spectrometer. Adhesive lap joint shear strength tests were conducted using a Withlab-WL2100C universal testing machine (UTM). Differential scanning calorimetry analysis for curing samples was tested using a Scinco-DSC N-650.

Synthesis of Ethyl 2,3-Dibromopropanoate (S3). To a solution of ethyl acrylate (10.63 mL, 99.88 mmol) in DCM (75 mL), bromine (5.14 mL, 99.88 mmol) was added dropwise at 0 °C for 20 min under an inert atmosphere. The reaction mixture was allowed to stir at 0 °C for 1 h and then at rt for 3 h. After completion of the reaction, the mixture was quenched with saturated Na₂S₂O₃ aqueous solution followed by extraction of the mixture with DCM and water, and then separation of the organic layer gave the dibromo compound in 95% yield (24.62 g). The analytical data for this compound were in excellent agreement with the reported data.⁵²

Synthesis of Ethyl 1-Benzylaziridine-2-carboxylate (S4). Ethyl 2,3-dibromopropanoate (15 g, 57.71 mmol) and trimethylamine (16 mL, 69.6 mmol) were sequentially added to a solution of benzylamine (6.184 mL, 57.71 mmol) in anhydrous ethanol (120 mL) at 0 °C under a N₂ atmosphere. The mixture was stirred at 60 °C for 1 h. The reaction solution was concentrated *in vacuo*, and the reaction

crude was extracted with DCM. The organic phase was dried with magnesium sulfate, and the solvent was removed under reduced pressure at room temperature. The resulting crude was purified by flash column chromatography to obtain the corresponding product in 92% yield (10.91 g) as a white solid. The analytical data for this compound were in excellent agreement with the reported data.⁵³

Synthesis of (1-Benzylaziridin-2-yl)methanol (S5). Lithium aluminum hydride (1.849 g, 48.72 mmol) was slowly added to a solution of ethyl 1-benzylaziridine-2-carboxylate (5 g, 24.36 mmol) in diethyl ether (130 mL). The mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with water (1.9 mL) and 15% NaOH aqueous solution (1.9 mL) and then water (5.6 mL). After the filtration of the mixture, the crude compound was extracted with ethyl acetate. The organic phase was dried with magnesium sulfate, and the solvent was removed under reduced pressure. The product was obtained in 87% yield (4.31 g) as a yellowish powder. The analytical data for this compound were in excellent agreement with the reported data.⁵⁴

Synthesis of (1-Benzylaziridin-2-yl)methyl 4-Methylbenzenesulfonate (S6). A solution of (1-benzylaziridin-2-yl)methanol (1 g, 6.127 mmol) in triethylamine (3.0 mL, 21.64 mmol) was added to a solution of *p*-toluenesulfonyl chloride (1.402 g, 7.352 mmol) in DCM (15 mL) at 0 °C under a N₂ atmosphere. The mixture was stirred at 0 °C for 2 h. The reaction crude was extracted with DCM. The organic phase was dried with magnesium sulfate, and the solvent was removed under reduced pressure at room temperature. The resulting crude was purified by flash column chromatography to obtain the corresponding product in 50% yield (973 mg) as a white solid. The analytical data for this compound were in excellent agreement with the reported data.⁵⁵

Synthesis of 2,2'-(((Propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1-benzylaziridine) (S1). (1-Benzylaziridin-2-yl)methyl 4-methylbenzenesulfonate (277 mg, 0.872 mmol) was added to a solution of bisphenol A (108 mg, 0.436 mmol), 18-crown-ether (15.5 mg, 0.0586 mmol), and KOH (135 mg, 2.398 mmol) in THF (15 mL). The mixture was refluxed for 17 h. The reaction solution was cooled to room temperature and extracted with DCM. The combined organic layer was dried over anhydrous MgSO₄, filtered off, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (EA:hexane = 2:1) to obtain the corresponding product in 44% yield (100 mg) as a yellowish oil. ¹H NMR (CDCl₃): δ 7.24–7.52 (m, 5H) 7.14 (d, *J* = 9.00 Hz, 2H) 6.82 (d, *J* = 8.60 Hz, 2H) 3.89–4.05 (m, 2H) 3.54 (td, *J* = 13.50, 8.60 Hz, 1H) 1.97–2.06 (m, 1H) 1.88 (d, *J* = 3.52 Hz, 1H) 1.66 (s, 3H) 1.60 (d, *J* = 6.65 Hz, 1H). ¹³C{¹H} NMR (CDCl₃): δ 156.4, 143.2, 138.8, 128.2, 127.9, 127.6, 127.0, 113.82, 70.0, 64.2, 41.6, 37.9, 32.0, 31.0. MS (ESI) *m/z*: [M + H]⁺ calcd for C₃₅H₃₉N₂O₂: 519.3012; found: 519.3009.

Synthesis of *N,N'*-(((Propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl))bis(4-methylbenzenesulfonamide) (S7). A mixture of potassium carbonate (6.09 g, 44.06 mmol), *p*-toluenesulfonamide (5.03 g, 29.37 mmol), diglycidyl ether of bisphenol A (5 g, 14.69 mmol), and 18-crown-6 (233 mg, 0.8814 mmol) in DMSO was heated at 100 °C with stirring for 2 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and washed with distilled water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (EA:hexane = 3:1) to obtain the corresponding product in 47% yield as white powder. ¹H NMR (CDCl₃): δ 7.75 (d, *J* = 8.24 Hz, 2 H) 7.31 (d, *J* = 8.55 Hz, 2 H) 7.11 (d, *J* = 8.85 Hz, 2 H) 6.75 (d, *J* = 8.85 Hz, 2 H) 4.82 (d, *J* = 5.19 Hz, 1 H) 4.08 (dd, *J* = 10.53, 6.26 Hz, 1 H) 3.89–3.96 (m, 2 H) 3.21–3.27 (m, 1 H) 3.04–3.13 (m, 1 H) 2.43 (s, 3 H) 1.62 (s, 3 H). ¹³C{¹H} NMR (CDCl₃): δ 155.93, 143.63, 143.54, 136.36, 129.76, 127.68, 127.03, 113.83, 69.20, 68.64, 45.51, 41.61, 30.90, 21.47. MS (ESI) *m/z*: [M + Na]⁺ calcd for C₃₅H₄₂N₂NaO₈S₂: 705.2280; found: 705.2276.

Synthesis of 2,2'-(((Propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1-tosylaziridine) (S2). To a solution of *N,N'*-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl))bis(4-methylbenzenesulfonamide) and triethylamine (120.9 mg, 1.195 mmol) in THF (5 mL) was added

methanesulfonyl chloride (40.3 mg, 0.3515 mmol) at 0 °C under a N₂ atmosphere. The mixture was heated at room temperature and stirred for 5 h. The reaction mixture was quenched with distilled water, and extractive work-up was performed with ethyl acetate. The combined organics were then washed with brine and dried over Na₂SO₄ and concentrated under reduced pressure. Without any purification, the mixture of crude product and potassium carbonate in acetonitrile was stirred at room temperature for 16 h. The reaction mixture was diluted with ethyl acetate and poured into distilled water, and extractive work-up was performed with ethyl acetate. The crude product was purified by flash column chromatography (EA:hexane = 1:2) to obtain the corresponding product in 72% yield as a white powder. ¹H NMR (CDCl₃): 7.83 (d, *J* = 8.24 Hz, 2 H) 7.32 (d, *J* = 7.93 Hz, 2 H) 7.06 (d, *J* = 8.85 Hz, 2 H) 6.63 (d, *J* = 8.85 Hz, 2 H) 3.84–4.07 (m, 2 H) 3.07–3.21 (m, 1 H) 2.78 (d, *J* = 7.02 Hz, 1 H) 2.44 (s, 3 H) 2.33 (d, *J* = 4.58 Hz, 1 H) 1.60 (s, 3 H). ¹³C{¹H} NMR (CDCl₃): δ 155.80, 144.60, 143.54, 134.57, 129.59, 127.99, 127.58, 113.71, 66.87, 41.57, 38.07, 31.03, 30.88, 21.59. MS (ESI) *m/z*: [M + Na]⁺ calcd for C₃₅H₃₈N₂NaO₆S₂: 669.2069; found: 669.2067.

¹H NMR Spectroscopic Analysis for the Kinetics of Ring-Opening Polymerization (ROP). The samples including resin (26 mM for Ts-DzEBA, 32 mM for Bn-DzEBA, and 49 mM for DGEBA) and 1:1 mole ratio of curing agents (DDDA, TPA, EDA, PDA, EDP, and HQ in Figure 3a) in DMSO-*d*₆ solution were prepared. The solution was reacted at 80 °C and monitored for 48 h. The conversion ratio (the ratio of ¹H NMR peak integration of product to that of initial resin) was estimated in ¹H NMR spectra measured at each reaction time. Figures S2–25 show these NMR spectra.

Differential Scanning Calorimetry (DSC) Analysis. For a typical experiment of nonisothermal DSC study, a mixture of resin and curing agent at 1:1 molar ratio weighed from 3 to 7 mg and enclosed in aluminum pan and lid was cured at various heating rates from 2 to 20 °C/min. Table S1 shows structures of curing agents conducted for DSC study and their melting point. Table S2 and Figures S27–S33 show these data.

Thermal Curing on Surface. A mixture of Bn-DzEBA (411 mg, 0.792 mmol) and dodecanedioic acid (182 mg, 0.792 mmol) was prepared by dissolving in 3 mL of tetrahydrofuran (THF). Polymer film was formed by the solvent-casting method: the prepared solution was cast into a Teflon dish (40 mm in diameter) and dried in air. The film was thermally cured at 80 °C for 3 h. The film was characterized with ATR FT-IR spectroscopy before and after curing.

Single Lap Shear Strength Test. An aluminum plate (100 mm × 25 mm × 0.3 mm) was degreased thoroughly with acetone and ethanol several times prior to application of resin and curing agent. A mixture of resin and curing agent (1:1 mole ratio; 0.11 M) was homogeneously coated on adhesive area (~500 mm²) of aluminum substrate by spin-coating (200 rpm, 15 s). Two aluminum plates were prepared in the same method and sandwiched as shown in Figure 5a. The resulting sample was thermally cured at different reaction times and temperatures. By use of a universal testing machine (UTM), shear strength was measured for each sample (Figures S34–S38).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00550.

Additional experimental images (Figures S1–S39), tables (Tables S1 and S2), and schemes (Schemes S1 and S2) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the NRF of Korea (NRF-2016R1D1A1A02937504; NRF-2017M3A7B8064518; NRF20100020209) and the Future Research Grant of Korea University. We thank Mr. Do Young Park and Prof. Cheol-Hong Cheon for kindly helping us to perform chiral HPLC analysis.

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