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Thermally Activated, Single Component Epoxy Systems

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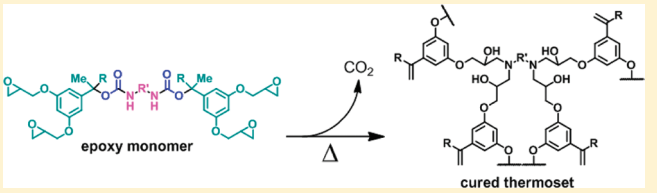
ABSTRACT: A single component epoxy system in which the resin and hardener components found in many two-component epoxies are combined onto the same molecule is described. The single molecule precursor to the epoxy resin contains both multiple epoxide moieties and a diamine held latent by thermally degradable carbamate linkages. These bis-carbamate "single molecule epoxies" have an essentially infinite shelf life and access a significant range in curing temperatures related to the structure of the carbamate linkages used.



INTRODUCTION

Epoxies are an important class of thermosetting polymers with diverse applications including adhesives, structural materials, paints, coatings, concrete, printed circuit boards, microelectronic encapsulation, the aerospace industry, and other consumer applications. In addition, recent interest has surfaced for using epoxies as self-healing materials,[1] chemical resists,[2] and composites with nanotubes.[3] The widespread utility of epoxy formulations can be explained by a combination of their exceptional processability prior to curing and their excellent postcure adhesion, mechanical strength and chemical resistance after curing. Additionally, the high-density three-dimensional network of epoxies makes them extremely robust materials, making them the thermoset of choice for many long-term applications.

The most common epoxy formulation consists of a multivalent epoxide ("resin") and multivalent amine ("hardener") to form a polymeric network of essentially infinite molecular weight. This reaction traditionally requires the two components to be stored separately and mixed immediately prior to use. Attempts to increase the amine latency traditionally take advantage of solubility or phase differences between the epoxy and the amine.[4−9] While these can still be packaged and marketed as single component systems, they have limitations most particularly with respect to shelf life. Additionally, amines can be made more latent through chemical modification, for example as their ketimine derivatives.[10−12] This strategy is indeed effective in increasing latency, but it requires rigorous processing to ensure that all components are water free due to the well-known lability of ketimines.

In the design of latent amine epoxies, we wanted to take advantage of the ability to block an amine with a thermally removable group. While the use of blocking agents is a strategy that has seen some recent and limited use in amine epoxies,[13,14] it has historically been much more prevalent in polyurethane chemistry.[15−19] Although blocking groups are effective in rendering a functional group unreactive until an appropriate stimulus is applied, most blocking agents once removed do not participate in the polyurethane cure. Typically the blocking agents remain as unreactive byproduct diluents, which can leach out over time and possibly present environmental or health problems. An alternative strategy is to use the blocking agent as the connecting linchpin between the hardener and resin. With this design, the atom economy of the curing reaction is increased and the production of toxic byproducts eliminated. Herein we describe such a strategy by using the susceptibility of the carbamate functional group to decompose under a thermal stimulus, and demonstrate its applicability toward the synthesis and characterization of "single component epoxies".

EXPERIMENTAL SECTION

Materials. All reagents were obtained from commercial sources and used without further purification unless otherwise noted. All solvents used were reagent grade (99.9%) unless otherwise noted. Tetrahydrofuran, toluene and dichloromethane were purified under argon by passing through two columns of neutral alumina on a commercial apparatus. Water was purified using a Barnstead NANOpure Diamond purification system.

Characterization. Elemental analysis was performed by the UC Berkeley analytical facilities. ^{1}H and ^{13}C NMR measurements were conducted on a Bruker AVB-400 nuclear magnetic resonance spectrometer. Differential scanning calorimetry (DSC) measurements were performed with a TA Instruments Q200 differential scanning calorimeter with standard aluminum pans. Monomers were used neat in all DSC experiments, with the exception of entry 1 of Table 1, where equimolar amounts of 1,6-diaminohexane and compound **10c** were mixed together prior to pan weighing. Ramped DSC scans were performed at a rate of 10 °C/min, and reported cure enthalpy values are an average of two measurements. Isothermal DSC analyses were performed by rapidly ramping the sample to the desired cure temperature before the starting time. Thermogravimetric analyses (TGA) were performed with a TA Instruments G5000 thermogravimetric analyzer, and were performed at a rate of 10 °C/min. Infrared spectra were taken with a Thermo Scientific Nicolet 6700 Fourier transform infrared spectrometer. Films were prepared by gently heating and stirring a mixture of the epoxy precursor in an 11 wt % poly(methacrylonitrile) solution in

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Table 1. Deprotection and Curing Characteristics for Epoxy Monomers and Model Compounds[a]

compound	TGA deprotection onset (°C)	DSC exotherm onset (°C)	maximum of DSC exotherm peak (°C)	enthalpy of cure (kJ/equiv of epoxide)	T_g (∞) (°C)
10c + 1,6-diaminohexane	-	58	74	105	112
12a	252	271	304	74	123
12b	222	239	265	87	-
13a	227	247	291	78	156
13b	176	192	222	89	-
22	211	220	236	85	114
23	170	174	205	93	163

[a] TGA and DSC data were obtained at a heating rate of 10 °C/min.

nitromethane until homogeneous, and then spin-coating onto NaCl disks at 1500 rpm for 60 s, drying at 90 °C for 15 min and placement in a vacuum desiccator until use. Relative peak ratios calculated using FTIR are an average of three films. Optical microscopy was performed with a Fisher Scientific Micromaster inverted digital microscope on samples with uniform (10 mm) thickness. Samples were cured at temperatures for time limits that were determined by isothermal DSC measurements with CO_2 evolution permitted.

Preparation of 3,5-Diglycidoxyacetophenone, 10a. To a solution of 3,5-dihydroxyacetophenone, **9a** (1.01 g, 6.65 mmol), in DMF (20 mL) was added epibromohydrin (2.20 mL, 26.6 mmol) followed by cesium carbonate (4.77 g, 14.6 mmol). This reaction was stirred overnight, after which 100 mL anhydrous ether was added to the reaction mixture. The organic layer was washed with 0.1 M NaOH, water, and brine and dried over anhydrous $MgSO_4$. Solvent was evaporated to yield 975 mg (53%) of a light yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.57 (s, 3H), 2.77−2.78 (dd, 2H), 2.92−2.94 (t, 2H), 3.36−3.39 (m, 2H), 3.93−3.97 (dd, 2H), 4.29−4.33 (dd, 2H), 6.72−6.73 (t, 1H), 7.13−7.14 (d, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.7, 44.5, 49.9, 69.0, 69.1, 106.5, 107.2, 139.0, 159.6, 197.4. IR ($CHCl_3$, cm^{-1}) 3051, 2970, 2923, 1684, 1595, 1444, 1363, 1298, 1177, 1156, 1063, 910. Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.6; H, 6.1. Found: C, 63.48, H, 5.99.

Preparation of 4-Glycidoxyacetophenone, 10b. To a solution of 4-hydroxyacetophenone, **9b** (3.67 g, 27.0 mmol), in dry DMF (50 mL) were added cesium carbonate (13.17 g, 40.4 mmol) and epibromohydrin (3.33 mL, 40.4 mmol). This reaction was stirred overnight, after which 250 mL water was added. The organics were extracted with ether, washed with 0.1 M NaOH and brine, dried over anhydrous magnesium sulfate, and solvents were removed in vacuo to yield 3.14 g (62%) of a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.56 (s, 3H), 2.77−2.79 (dd, 1H), 2.92−2.94 (dd, 1H), 3.36−3.39 (m, 1H), 3.97−4.02 (dd, 1H), 4.30−4.34 (dd, 1H), 6.95−6.97 (d, 2H), 7.92−7.95 (d, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.39, 44.59, 49.91, 68.88, 114.29, 130.62, 162.29, 196.74. IR ($CHCl_3$, cm^{-1}): 3061, 3003, 2930, 1684, 1676, 1598, 1510, 1420, 1360, 1271, 1243, 1176, 1026, 959, 915. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.7; H, 6.3. Found: C, 68.43; H, 6.12.

Preparation of 2-(3,5-Diglycidoxyphenyl)propene, 10c. A methyltriphenylphosphine bromide (1.66 g, 4.66 mmol) in dry THF (25 mL) was cooled to −78 °C, and *n*-butyllithium (2.5 M in hexanes, 4.66 mmol) was added dropwise. After 10 min, a solution of acetophenone **10a** (1.23 g, 4.66 mmol) in dry THF was added dropwise, and the solution was allowed to stir at room temperature for 12 h. The mixture was then filtered through a plug of Celite, concentrated in vacuo, and purified via silica gel chromatography (1:10−1:4 ethyl acetate in hexanes). Solvents were removed to yield 285 mg (23%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.11 (s, 3H), 2.75−2.77 (dd, 2H), 2.90−2.92 (t, 2H), 3.34−3.36 (m, 2H), 3.93−3.97 (dd, 2H), 4.21−4.24 (dd, 2H), 5.08 (s, 1H), 5.34 (s, 1H), 6.44−6.45 (t, 1H), 6.65−6.66 (d, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.1, 45.0, 50.4, 69.1, 100.9, 105.5, 113.3, 143.3, 143.9, 159.7. IR ($CHCl_3$, cm^{-1}) 3084, 2926, 1770, 1593, 1435, 1346, 1253, 1176, 1131, 1063, 909. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.7, H, 6.9. Found: C, 68.75, H, 7.01.

Preparation of 1-(3,5-Diglycidoxyphenyl)ethanol, 11a. A solution of acetophenone **10a** (6.96 g, 26.3 mmol) in THF (50 mL) and methanol (100 mL) was cooled to 0 °C, and then sodium borohydride (1.99 g, 52.7 mmol) was added. The reaction was allowed to stir at room temperature for 2 h, at which point starting material was completely consumed by thin layer chromatography (1:1 ethyl acetate:hexanes) and the reaction was quenched with aqueous 1 M $NaHSO_4$. The mixture was concentrated and extracted with diethyl ether. The organic portion was washed with brine, dried over magnesium sulfate, and solvent was removed to afford 6.28 g (89%) of a light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.48−1.50 (d, 3H), 2.32 (br s, 1H), 2.78−2.80 (t, 2H), 2.93−2.95 (t, 2H), 3.36−3.39 (m, 2H), 3.74−3.83 (dd, 2H), 4.17−4.21 (dd, 2H), 4.83−4.88 (q, 1H), 6.44 (s, 1H), 6.60 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.2, 44.7, 50.1, 68.8, 70.3, 100.6, 104.5, 148.8, 159.7. IR (neat, cm^{-1}): 3422, 2973, 2928, 2876, 1601, 1449, 1346, 1294, 1176, 1131, 1055, 909. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.2; H, 6.8. Found: C, 62.89; H, 7.07.

Preparation of 1-(4-Glycidoxyphenyl)ethanol, 11b. A solution of acetophenone **10b** (3.10 g, 16.1 mmol) in methanol (50 mL) was cooled to 0 °C, and then sodium borohydride (1.20 g, 32.3 mmol) was added. The reaction was allowed to stir at room temperature for 2 h, at which point starting material was completely consumed by thin layer chromatography (1:1 ethyl acetate:hexanes) and the reaction was quenched with aqueous 1 M $NaHSO_4$. The mixture was concentrated and extracted with diethyl ether. The organic portion was washed with brine, dried over magnesium sulfate, and solvent was removed to afford 3.02 g (96%) of a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.51−1.52 (d, 3H), 1.76 (br s, 1H), 2.79−2.81 (dd, 1H), 2.93−2.96 (dd, 1H), 3.37−3.41 (m, 1H), 3.98−4.02 (dd, 1H), 4.24−4.28 (dd, 1H), 4.87−4.92 (q, 1H), 6.92−6.96 (d, 2H), 7.32−7.34 (d, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.1, 44.8, 50.2, 68.8, 70.0, 114.6, 126.7, 138.6, 157.9. IR (neat, cm^{-1}): 3404, 2971, 2925, 1610, 1513, 1453, 1241, 1178, 1088, 1035, 902. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.0; H, 7.26. Found: C, 67.75; H, 7.28.

Preparation of *N,N′*-Bis[[1-(3,5-diglycidoxyphenyl)ethoxy]-carbonyl]hexane-1,6-diamine, 12a. The alcohol **11a** (2.0 g, 7.68 mmol) and 1,6-diisocyanatohexane (968 mg, 5.76 mmol) were added to 3 mL of toluene in a microwave reaction vial. The reaction was heated to 120 °C for 5 h in microwave, at which time no starting material was observed via thin layer chromatography (2:1 ethyl acetate:-hexanes). The entire reaction contents were purified with silica gel chromatography (1:1 to 3:1 ethyl acetate:hexanes). Solvent was removed in vacuo to yield 954 mg (35%) of a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28 (br s, 4H), 1.45−1.47 (d, 10 H), 2.72−2.74 (dd, 4H), 2.87−2.89 (t, 3.85), 3.11−3.12 (br d, 4H), 3.31−3.33 (dd, 4H), 3.87−3.91 (dd, 4H), 4.18−4.20 (d, 4H), 4.83 (br s, 2H), 5.64−5.68 (q, 2H),

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6.39 (s, 2H), 6.50−6.51 (d, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.7, 26.3, 30.0, 40.9, 44.8, 50.2, 69.0, 72.4, 100.7, 105.3, 145.2, 156.0, 159.8. IR (neat, cm^{-1}): 3341, 2979, 2931, 2861, 1707, 1599, 1529, 1450, 1355, 1262, 1178, 1050, 910. Anal. Calcd for $C_{36}H_{48}N_2O_{12}$: C, 61.7; H, 6.9; N, 4.0. Found: 61.84; H, 6.79; N, 4.10.

Preparation of *N,N′*-Bis[[1-(4-glycidoxyphenyl)ethoxy]-carbonyl]hexane-1,6-diamine, 12b. The alcohol **11b** (1 g, 5.15 mmol) and 1,6-diisocyanatohexane (519 mg, 3.09 mmol) were added to 3 mL toluene. This mixture was heated to 90 °C and stirred overnight. The reaction was purified via silica gel chromatography (1:1 ethyl acetate:-hexane) to yield 871 mg (61%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28 (br s, 4H), 1.45 (br s, 4H), 1.49−1.51 (d, 6H), 2.74−2.75 (dd, 2H), 2.89−2.91 (t, 2H), 3.09−3.15 (m, 4H), 3.32−3.36 (m, 2H), 3.92−3.95 (dd, 2H), 4.19−4.22 (dd, 2H), 4.69 (s, 2H), 5.71−5.76 (q, 2H), 6.87−6.89 (d, 4H), 7.25−7.29 (d, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.3, 26.4, 30.0, 40.9, 44.9, 50.3, 68.9, 72.3, 114.7, 127.7, 135.1, 156.2, 158.2. IR ($CHCl_3$, cm^{-1}): 3340, 2931, 1701, 1612, 1514, 1242, 1179, 1063, 1034, 912. Anal. Calcd for $C_{30}H_{40}N_2O_8$: C, 64.7; H, 7.2; N, 5.0. Found: C, 64.74; H, 7.24; N, 5.28.

Preparation of *N,N′*-Bis[[1-(3,5-diglycidoxyphenyl)ethoxy]-carbonyl]toluene-2,4-diamine, 13a. The alcohol **11a** (1.05 g, 3.94 mmol) and 2,4-tolylenediisocyanate (343 mg, 1.97 mmol) were added to dry toluene (3 mL) and heated to 90 °C overnight. The entire contents were purified via silica gel chromatography (1:1 to 3:1 ethyl acetate:hexanes). Solvent was removed in vacuo to yield 510 mg (36%) of a colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.52−1.56 (dd, 6H), 2.18 (s, 3H), 2.74−2.75 (m, 4H), 2.89−2.91 (m, 4H), 3.32−3.36 (m, 4H), 3.89−3.93 (m, 4H), 4.19−4.23 (m, 4H), 5.74−5.80 (m, 2H), 6.40−6.43 (m, 2H), 6.51 (br s, 1H), 6.55−6.56 (m, 4H), 6.81 (br s, 1H), 7.03−7.05 (d, 1H), 7.18−7.20 (d, 1H), 7.77 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.1, 22.4, 22.6, 25.3, 44.8, 50.2, 68.9, 70.4, 101.0, 104.6, 105.2, 105.3, 105.4, 105.5, 130.9, 159.8. IR ($CHCl_3$, cm^{-1}): 2917, 1721, 1598, 1530, 1446, 1224, 1177, 1046, 904. Anal. Calcd for $C_{37}H_{42}N_2O_{12}$: C, 62.9; H, 6.0; N, 4.0. Found: C, 62.62; H, 6.12; N, 3.60.

Preparation of *N,N′*-Bis[[1-(4-glycidoxyphenyl)ethoxy]-carbonyl]toluene-2,4-diamine, 13b. The alcohol **11b** (1 g, 5.15 mmol) and tolylene 2,4-diisocyanate (538 mg, 3.09 mmol) were added to 3 mL toluene. This mixture was heated to 90 °C and stirred overnight. The reaction was purified via silica gel chromatography (1:1 ethyl acetate: hexane) to yield 341 mg (24%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55−1.60 (m, 6H), 2.16 (s, 3H), 2.74−2.76 (dd, 2H), 2.89−2.92 (m, 2H), 3.34−3.36 (m, 2H), 3.94−3.98 (dd, 2H), 4.19−4.24 (m, 2H), 5.82−5.88 (d, 2H), 6.39 (s, 1H), 6.58 (s, 1H), 6.88−6.92 (m, 4H), 7.02−7.04 (d, 1H), 7.18 (br s, 1H), 7.30−7.34 (t, 4H), 7.77 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.2, 22.1, 22.3, 44.9, 50.3, 69.0, 73.3, 109.4, 114.9, 127.8, 127.9, 130.9, 134.6, 136.9, 153.2, 158.5, 164.2. IR ($CHCl_3$, cm^{-1}): 3320, 2980, 2922, 1718, 1611, 1514, 1227, 1179, 1063, 1035, 913. Anal. Calcd for $C_{31}H_{34}N_2O_8$: C, 66.2; H, 6.1; N, 5.0. Found: C, 65.82; H, 5.96; N, 5.21.

Preparation of *N,N′*-Bis[[1-(4-methoxyphenyl)ethoxy]-carbonyl]hexane-1,6-diamine, 14. To a solution of 1-(4-Methoxyphenyl)ethanol (1.04 g, 6.82 mmol) in dry toluene (3 mL) was added 1,6-diisocyanatohexane (690 mg, 4.11 mmol). This reaction was heated at 90 °C for 10 h, and then purified via silica gel chromatography (1:2 to 2:1 ethyl acetate:hexanes) to yield 986 mg (61%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26−1.29 (m, 4H), 1.42−1.46 (m, 4H), 1.50−1.52 (d, 6H), 3.10−3.15 (m, 4H), 3.79 (s, 6H), 4.70 (br s, 2H), 5.74−5.75 (q, 2H), 6.86−6.88 (d, 4H), 7.27−7.29 (d, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.3, 26.4, 30.0, 55.4, 72.4, 113.9, 127.6, 134.5, 156.2, 159.3. IR ($CHCl_3$, cm^{-1}): 3552, 2933, 1700, 1614, 1516, 1247, 1178, 1065, 1035. Anal. Calcd for $C_{26}H_{36}O_6$: C, 66.1; H, 7.7; N, 5.9. Found: C, 66.36; H, 7.74; N, 6.07.

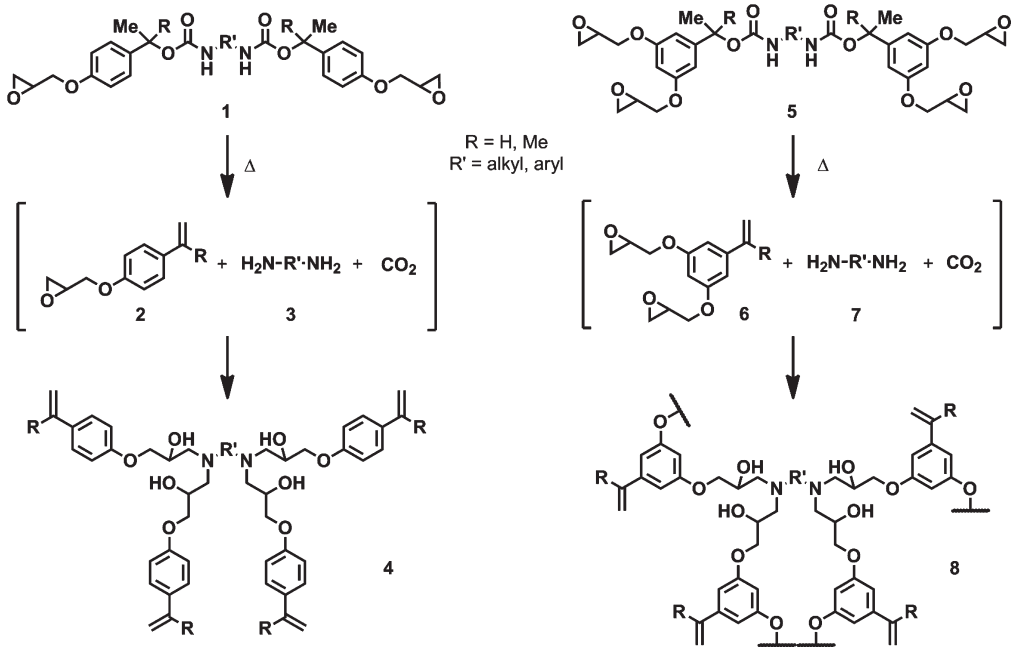
Preparation of Methyl 3,5-Diallyloxybenzoate, 16. To a solution of methyl 3,5-dihydroxybenzoate, **15** (5 g, 29.7 mmol), in dry DMF (50 mL) was added potassium carbonate (12.3 g, 89.1 mmol) and allyl bromide (4.66 mL, 74.3 mmol). This reaction was stirred overnight, after which 250 mL diethyl ether was added, and the organic layer was washed with 0.1 M NaOH, brine, and dried over magnesium sulfate. Solvent was removed in vacuo and recrystallized in ethyl acetate and hexanes to yield 6.7 g (91%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.90 (s, 3H), 4.54−4.55 (d, 4H), 5.28−5.31 (d, 2H), 5.40−5.44 (d, 2H), 6.01−6.05 (m, 2H), 6.69 (s, 1H), 7.20 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.26, 69.04, 107.12, 108.12, 117.94, 131.94, 132.81, 159.57, 166.79. IR ($CHCl_3$, cm^{-1}): 2973, 1723, 1597, 1446, 1323, 1301, 1235, 1168, 1053, 930. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.7; H, 6.5. Found: C, 67.74; H, 6.53.

Preparation of 1-(3,5-Diallyloxyphenyl)-1-methylethanol, 17. To a solution of the preceding methyl ester **16** (6.4 g, 25.9 mmol) in dry THF (100 mL) was added a 3 M solution of methylmagnesium bromide in ether (19 mL, 57 mmol). This reaction was stirred overnight and quenched with saturated aqueous ammonium chloride. The mixture was concentrated and extracted with diethyl ether. The organic layers were combined, washed with brine, and dried over magnesium sulfate. Solvent was removed in vacuo, and was purified via silica gel chromatography, eluting with 1:3 ethyl acetate:hexanes to yield 4.7 g (73%) of a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.53 (s, 6H), 2.18 (s, 1H), 4.49−4.51 (dt, 4H), 5.25−5.29 (dq, 2H), 5.38−5.43 (dq, 2H), 5.99−6.09 (m, 2H), 6.37−6.38 (t, 1H), 6.65−6.66 (d, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 31.7, 68.9, 72.6, 99.8, 104.0, 117.8, 133.3, 152.0, 159.6. IR (neat, cm^{-1}) 3415, 2977, 1595, 1438, 1423, 1362, 1293, 1166, 1053, 927. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.6; H, 8.1. Found: C, 72.22; H, 8.10.

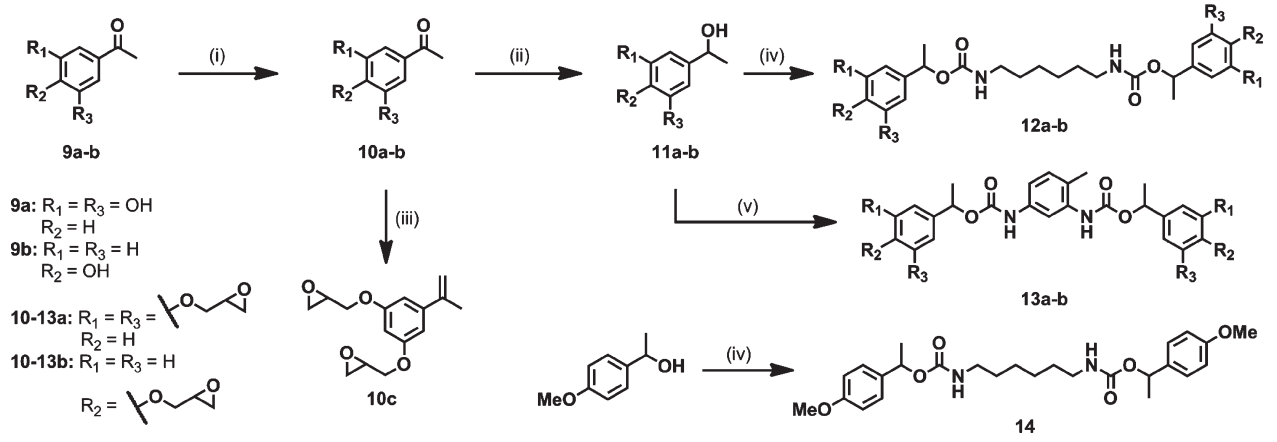
Preparation of *N,N′*-Bis[[1-(3,5-diallyloxyphenyl)-1-methylethoxy]carbonyl]hexane-1,6-diamine, 18. The alcohol **17** (9.67 g, 39.0 mmol) was added to 30 mL of dry tetrahydrofuran. A solution of 1.6 M methyllithium in ether (2.44 mL, 3.90 mmol) was added dropwise, and the resulting solution was heated to reflux for 1 h. The reaction was cooled to room temperature, and a solution of 1, 6-diisocyanatohexane (3.91 g, 23.3 mmol) in 20 mL tetrahydrofuran was added dropwise via addition funnel. The reaction was heated back to reflux overnight, after which it was cooled to room temperature and concentrated. The residue was dissolved in ethyl acetate, washed with water, dried, and purified via silica gel chromatography (1:2 ethyl acetate:hexane) to yield 3.86 g (30%) of a clear oil that solidified over time. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28 (br s, 4H), 1.43 (br s, 4H), 1.71 (s, 12H), 3.05−3.07 (d, 4H), 4.48−4.50 (dt, 8H), 4.76−4.77 (d, 2H), 5.25−5.29 (dq, 4H), 5.37−5.43 (dq, 4H), 5.99−6.09 (m, 4H), 6.36−6.37 (t, 2H), 6.53−6.54 (d, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.3, 29.1, 30.0, 40.4, 68.9, 80.4, 99.6, 104.0, 117.8, 133.4, 149.4, 149.4, 155.2, 159.6. IR ($CHCl_3$, cm^{-1}): 3348, 2980, 2932, 2860, 1701, 1596, 1521, 1448, 1363, 1260, 1149, 1053, 928. Anal. Calcd for $C_{38}H_{52}N_2O_8$: C, 68.6; H, 7.9; N, 4.2. Found: C, 68.49, H, 7.96; N, 4.54.

Preparation of *N,N′*-Bis[[1-(3,5-diallyloxyphenyl)-1-methylethoxy]carbonyl]toluene-2,4-diamine, 19. Methyllithium (756 uL, 1.6 M) was added to a solution of the alcohol **17** (3 g, 12.1 mmol) in dry tetrahydrofuran (20 mL). This was heated to reflux for 1 h, then allowed to cool to room temperature before cooling on an ice bath. A solution of tolylene 2,4-diisocyanate (1.26 g, 7.26 mmol) in dry tetrahydrofuran (10 mL) was added dropwise to the reaction mixture. After addition was complete, the reaction was heated to reflux overnight. The mixture was concentrated, and the resulting residue was extracted with ethyl acetate, washed, dried, evaporated, and purified via silica gel chromatography (1:2 to 1:1 ethyl acetate:hexane) to yield 1.523 (38%) of a clear oil that had traces of starting material. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.74 (s, 6H), 1.78 (s, 6H), 2.18 (s, 3H), 4.47−4.54 (m, 8H), 5.23−5.29 (m, 4H), 5.36−5.43 (m, 4H), 6.00−6.05 (m, 4H), 6.36−6.37 (t, 1H), 6.38 (t, 1H), 6.44 (br s, 1H), 6.54−6.57 (dd, 4H), 6.66−6.67 (d, 2H), 7.00−7.02 (d, 1H), 7.59 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.1, 28.9, 31.7, 53.5, 68.9, 72.7, 81.7, 99.7, 99.8, 103.9, 104.0, 117.7, 117.8, 130.7, 133.3, 136.3, 136.9, 148.6,

Scheme 1. Overview of Thermal Deprotection and Curing of Model Compound 1 and Epoxy Precursor 5 To Give Oligomer 4 and Cross-Linked Epoxy 8



Scheme 2. Synthesis of Secondary Benzylic Epoxy Precursors 12 and 13 and Non-Curing Control Precursor 14[a]



[a] Reagents and conditions: (i) epibromohydrin, Cs_2CO_3, DMF; (ii) $NaBH_4$, MeOH/THF; (iii) CH_3PH_3PBr, *n*-BuLi, THF; (iv) 1,6-diisocyanatohexane, toluene; (v) 2,4-tolylene diisocyanate, toluene.

148.7, 151.9, 159.6, 159.7. IR ($CHCl_3$, cm^{-1}): 2982, 1712, 1597, 1528, 1449, 1166, 1142, 1054, 927. Anal. Calcd for $C_{38}H_{52}N_2O_8$: C, 69.8; H, 6.9; N, 4.2. Found: C, 70.3, H, 7.5; N, 2.9.

Preparation of *N,N′*-Bis[[1-(3,5-dihydroxyphenyl)-1-methylethoxy]carbonyl]hexane-1,6-diamine, 20. The bis-dicarbamate **18** (1.36 g, 2.04 mmol) was dissolved in methanol (12 mL) and tetrahydrofuran (22 mL). Tetrakis(triphenylphosphino)palladium (231 mg, 0.20 mmol) was added, and the solution was cooled in an ice bath before adding sodium borohydride (771 mg, 20.4 mmol). This was stirred for 4 h before thin layer chromatography (2:1 ethyl acetate:hexane) showed reaction completion. The reaction was quenched with sodium bisulfate and concentrated. The residue was extracted with ethyl acetate, and the combined extracts were washed, dried, and evaporated, purified via silica gel chromatography (1:1 to 5:1 ethyl acetate:hexane), and finally triturated with CH_2Cl_2, ethyl acetate, and hexanes to give 978 mg (95%) of a light tan solid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.19 (br s, 4H), 1.33 (br s, 4H), 1.57 (s, 12 H), 2.84−2.85 (q, 4H), 6.05−6.06 (t, 2H), 6.17 (d, 4H), 6.95−6.98 (t, 2H), 9.08 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 14.6, 26.5, 29.6, 29.9, 79.3, 101.1, 103.1, 149.8, 155.3, 158.4. IR (KBr, cm^{-1}): 3343, 2976, 2928, 1684, 1597, 1516, 1441, 1332, 1266, 1139, 996, 959. Anal. Calcd for $C_{26}H_{36}N_2O_8$: C, 61.9; H, 7.2; N, 5.6. Found: C, 61.87; H, 7.29; N, 5.55.

Preparation of *N,N′*-Bis[[1-(3,5-hydroxyphenyl)-1-methylethoxy]-carbonyl]toluene-2,4-diamine, 21. The bis-carbamate **19** (1.5 g, 2.2 mmol) was added to tetrahydrofuran (25 mL) and methanol (20 mL). Tetrakis(triphenylphosphino)palladium (2.07 g, 0.179 mmol) was added, and the solution was cooled to 0 °C before adding sodium borohydride (500 mg, 13.2 mmol). This reaction was stirred for 2 h, when it was quenched with saturated aqueous ammonium chloride, concentrated,

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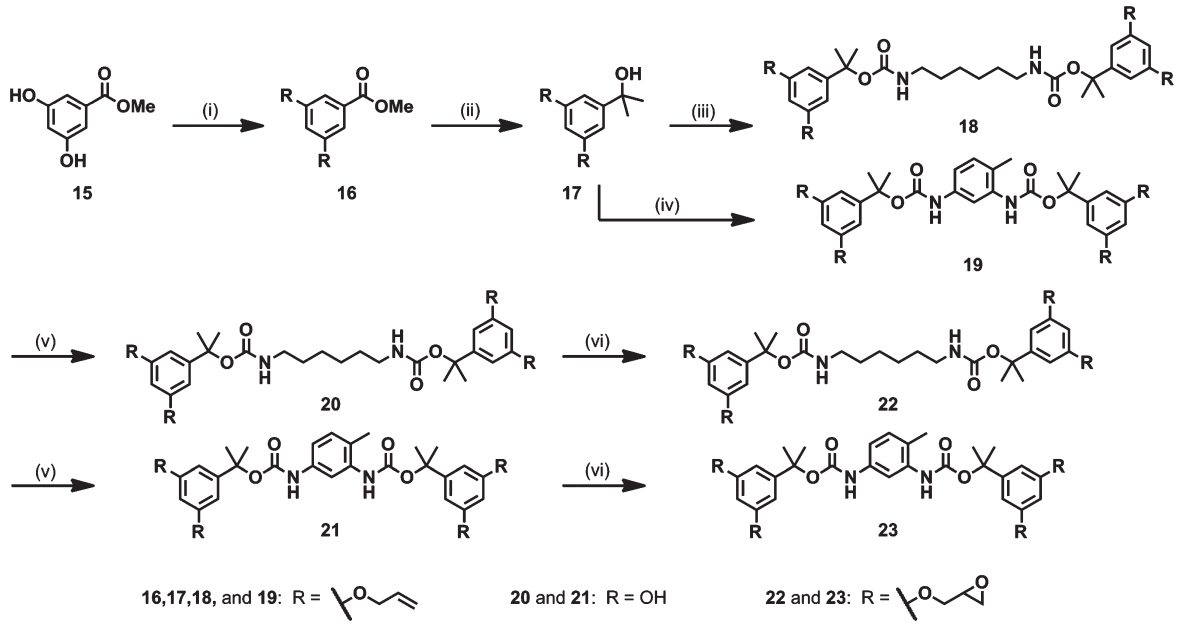
Scheme 3. Synthesis of Tertiary Benzylic Epoxy Precursors 22 and 23[a]



[a] Reagents and conditions: (i) allyl bromide, K_2CO_3, DMF; (ii) methylmagnesium bromide, THF; (iii) 1,6-diisocyanatohexane, cat. methyllithium, THF; (iv) 2,4-tolylene diisocyanate, cat. methyllithium, THF; (v) $Pd(PPH_3)_4$, $NaBH_4$, MeOH/THF; (vi) epibromohydrin, Cs_2CO_3, DMF.

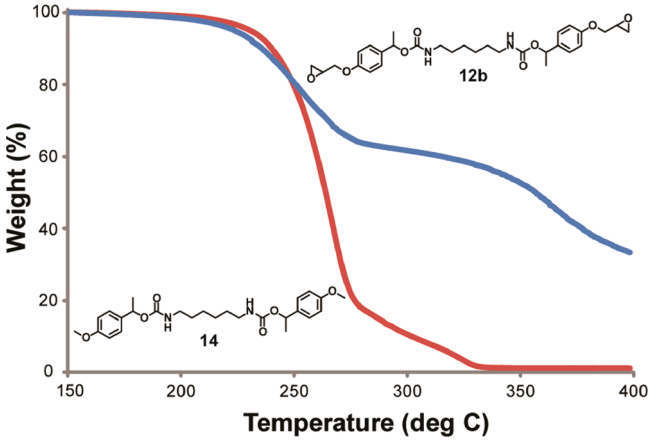


Figure 1. Comparison of TGA traces for monomer **12b** (blue) and control **14** (red).

and extracted with ethyl acetate. The combined extracts were washed, dried, evaporated, and purified via silica gel chromatography (1:1 to 5:1 ethyl acetate:hexanes) to yield a dark oil that was triturated with ethyl acetate, CH_2Cl_2, and hexanes to yield 900 mg (78%) of an off-white solid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.64 (s, 12H), 2.09 (s, 3H), 6.06−6.07 (q, 2H), 6.22−6.24 (dd, 4H), 6.97−6.99 (d, 1H), 7.07−7.10 (d, 1H), 7.40 (s, 1H), 8.63 (br s, 1H), 9.12 (s, 2H), 9.13 (s, 2H), 9.44 (br s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 17.2, 20.8, 29.1, 31.2, 70.5, 79.9, 100.1, 100.8, 100.9, 102.5, 102.6, 103.0, 114.6, 125.3, 130.0, 136.6, 137.4, 148.7, 148.9, 152.0, 152.7, 152.9, 157.8, 158.0, 158.1. IR (KBr, cm^{-1}): 3295, 2967, 1683, 1587, 1432, 1227, 1125, 1037, 993, 958. Anal. Calcd for $C_{27}H_{30}N_2O_8$: C, 63.5; H, 5.9; N, 5.4. Found: C, 63.29; H, 6.12; N, 5.29.

Preparation of *N,N′*-Bis[[1-(3,5-diglycidoxyphenyl)-1-methylethoxy]carbonyl]hexane-1,6-diamine, 22. A 10 mL aliquot of dry *N,N′*-dimethylformamide was added to the tetrahydroxybis-carbamate **20** (900 mg, 1.80 mmol) and cesium carbonate (2.85 g, 7.39 mmol). Epibromohydrin (4.93 g, 36 mmol) was then added, and the reaction was stirred overnight. The reaction was diluted with water and extracted with diethyl ether. The combined extracts were washed with 0.1 M aqueous NaOH, dried, evaporated, and purified via silica gel chromatography, eluting with 2:1 CH_2Cl_2:ethyl acetate, to yield 600 mg (45%) of a light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.27 (br s, 4H), 1.43 (br s, 4H), 1.70 (s, 12H), 2.72−2.74 (dd, 4H), 2.88−2.90 (t, 4H), 3.05−3.06 (br d, 4H), 3.31−3.34 (m, 4H), 3.89−3.93 (dd, 4H), 4.16−4.19 (dd, 4H), 4.80 (br s, 2H), 6.37 (s, 2H), 6.55−6.56 (d, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.2, 29.0, 30.0, 40.4, 44.8, 50.1, 68.8, 80.2, 99.4, 104.2, 149.6, 155.2, 159.4. IR ($CHCl_3$, cm^{-1}): 3362, 2980, 2931, 1711, 1597, 1521, 1448, 1257, 1176, 1153, 1058, 912. Anal. Calcd for $C_{38}H_{52}N_2O_{12}$: C, 62.6; H, 7.2; N, 3.8. Found: C, 62.74; H, 7.43; N, 3.67.

Preparation of *N,N′*-Bis[[1-(3,5-diglycidoxyphenyl)-1-methylethoxy]carbonyl]toluene-2,4-diamine, 23. Dry *N,N′*-dimethylformamide (2 mL) was added to the tetrahydroxy bis-carbamate **21** (750 mg, 1.46 mmol) and cesium carbonate (2.26 g, 5.86 mmol) under nitrogen atmosphere. Epibromohydrin (2.9 mL, 35.2 mmol) was added via syringe, and the mixture was stirred for 48 h. The mixture was then diluted with water and extracted with diethyl ether. The combined extracts were washed with water, dried, evaporated, and purified via silica gel chromatography (1:20 to 1:5 ethyl acetate:dichloromethane) to yield 575 mg (53%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.74−1.78 (d, 12H), 2.19 (s, 3H), 2.73−2.74 (m, 4H), 2.87−2.89 (m, 4H), 3.31−3.33 (m, 4H), 3.91−3.93 (m, 4H), 4.15−4.21 (m, 4H), 6.36−6.40 (dt, 2H), 6.46 (br s, 1H), 6.56−6.60 (dd, 4H), 6.65 (br s, 1H), 7.00−7.02 (d, 2H), 7.22 (br s, 1H), 7.59 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.9, 29.0, 44.9, 50.3, 68.9, 69.0, 99.8, 99.9, 104.3, 104.4, 130.9, 136.4, 137.0, 149.1, 149.0, 149.1, 159.6, 159.7. IR ($CHCl_3$, cm^{-1}): 3340, 2983, 2928, 1729, 1598, 1530, 1448, 1232, 1176, 1138, 1051, 910. Anal. Calcd for $C_{39}H_{46}N_2O_{12}$: C, 63.7; H, 6.3; N, 3.8. Found: C, 63.45; H, 6.51; N, 3.92.

RESULTS AND DISCUSSION

The synthetic design of these single component amine epoxy precursors are inspired by previous work with a carbamate deprotection mechanism using ultraviolet light as the trigger.[20−25]

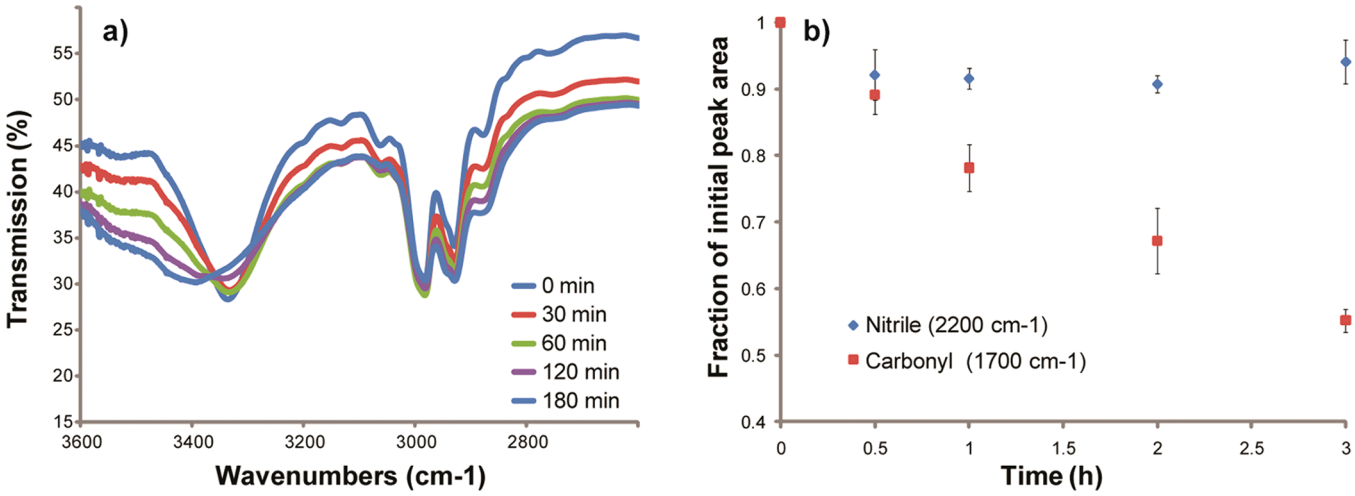


Figure 2. (a) Selected IR spectra of films and (b) relative peak ratios of carbonyl and nitrile stretches of precursor **13b** (as a 200 mM solution in a mixture of 11% poly(methacrylonitrile) in nitromethane) as a function of curing times at 160 °C.

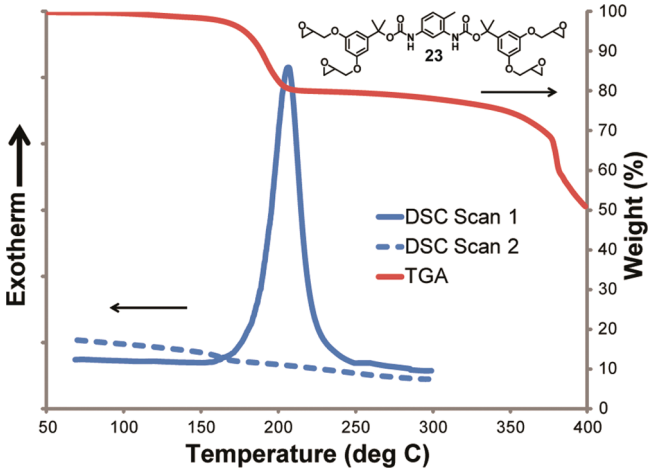


Figure 3. Combined DSC and TGA traces for monomer **23**.

Rather than using this motif as a UV-curable system, which operates at an inefficient wavelength for large-scale use (280 nm) and has a poor quantum yield (with many deleterious side reactions), we decided to take advantage of the thermal instability of the carbamate functional group.[19] The overall process of thermal deprotection and curing of our "single component epoxies" is summarized in Scheme 1. In contrast to phenyl carbamate, the functionality commonly used in a blocked isocyanate, which thermally decomposes into an isocyanate and a phenol, the carbamate moieties of our epoxy precursors (e.g., **1** and **5**) are designed to undergo the entropically favorable thermal decomposition to yield carbon dioxide, an eliminated alkene (**2** and **6**), and a primary diamine (**3** and **7**). Because the eliminated alkene contains at least one epoxide moiety, it can react with the newly formed primary amine, thus realizing the key step in the formation of an epoxy thermoset. In practice, the epoxy precursor should contain at least two latent amines and four epoxy moieties (such as **5**) in order to produce a cross-linked epoxy thermoset. Epoxy precursors that have a low epoxy/amine ratio and cannot cross-link (such as **1**) were still used as model compounds to illustrate the structure/function relationship between molecular design and deprotection temperature.

The synthetic route to access these epoxy precursors depends upon the degree of substitution of the benzylic carbon. Scheme 2 outlines the preparation of bis-carbamate epoxy precursors **13** and **15**, which are derived from a secondary benzylic alcohol in a facile three-step process. For example, **13a** is prepared from 3, 5-dihydroxyacetophenone, **9a**, by alkylation with epibromohydrin in the presence of cesium carbonate to afford **10a** followed by reduction with sodium borohydride and bis-carbamation with a diisocyanate to yield the desired secondary bis-carbamate.

In the case of tertiary bis-carbamates **22** and **23**, the synthetic sequence starting from methyl 3,5-dihydroxybenzoate is somewhat lengthier requiring five steps due to the need for a protection—deprotection sequence (Scheme 3). The starting material **15** was first bis-allylated to afford **16,** which was then treated with two equivalents of methylmagnesium bromide to afford the tertiary benzylic alcohol **17**. Allyl protection of the phenols of **15** was crucial to enable the selective methyllithium-catalyzed bis-carbamation of the tertiary alcohol to produce alkyl bis-carbamate **18** and aryl bis-carbamate **19**. The allyl groups were then removed via palladium-catalyzed sodium borohydride reduction to give the hydroxylated bis-carbamates **20** and **21**. Finally, four epoxide groups were installed using epibromohydrin and cesium carbonate to afford the desired epoxies **22** and **23**. Direct epoxidation of the allyl groups using conventional reagents (mCPBA or DMDO) were unsuccessful. Although the two synthetic pathways differ in length and ease of preparation, the overall synthetic scheme has flexibility with respect to the substitution of the benzylic carbon, the substitution around the phenyl ring, and the nature of the diisocyanate. This flexibility allowed access to a small library of epoxy precursors with a significant range of deprotection and curing temperatures.

When heated past the deprotection temperature of the carbamate moiety, the epoxy precursors display a decomposition with two inflection points. TGA monitoring confirmed the first inflection, corresponding to the weight change expected from the loss of 2 CO_2 molecules from the epoxy material, as well as some evaporation of the diamine and glycidyl ether formed postdeprotection. Following initial weight loss, the weight of the sample subjected to TGA analysis only decreases slowly, likely as a result of evaporation, until the second inflection point occurs at an elevated temperature (>350 °C). Only bis-carbamates that include

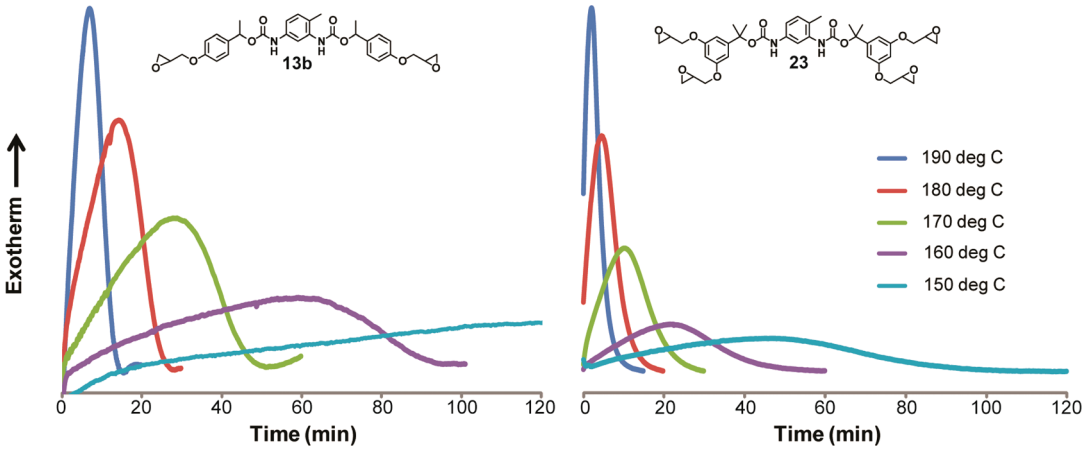


Figure 4. DSC isothermal comparison of monomers **13b** and **23**.

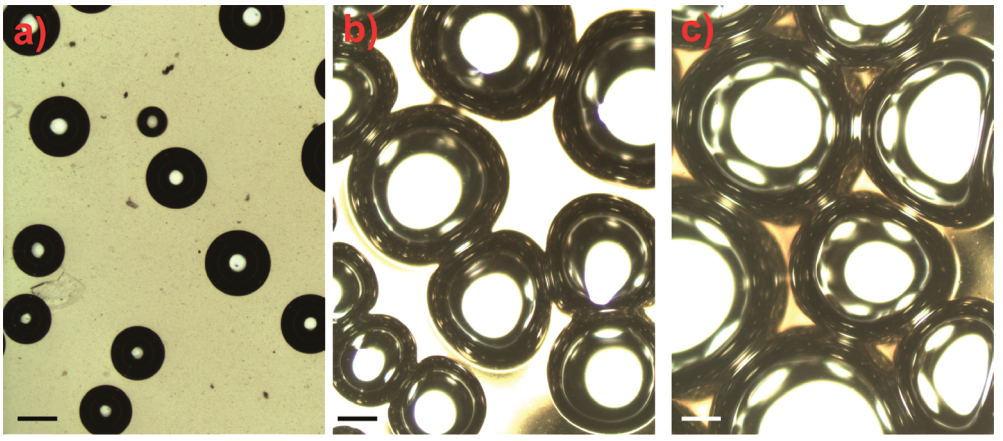


Figure 5. Comparison of CO_2 bubbles produced in cured resins of epoxy **23**, cured fully at different temperatures: (a) 160 °C for 1 h; (b) 180 °C for 30 min; (c) 200 °C for 15 min. Scale bar is 200 μm.

epoxy groups displayed this relative stability after loss of CO_2, as seen by TGA comparison between epoxy **12b** and **14** (Figure 1). The control epoxy **14** was designed to release CO_2 at a similar temperature as epoxy **12b**, but without the ability to cure. IR monitoring of the deprotection of epoxy precursor **13b** diluted in a matrix of poly(methacrylonitrile) heated to 160 °C (Figure 2) shows that the carbamate NH peak at 3329 cm^{-1} is replaced by a broader peak centered at 3386 cm^{-1}, primarily due to the amine of the deprotected monomer. Although this precursor is diluted in a polymer matrix, it is possible that background curing may give rise to hydroxyls in this region of the spectrum. In addition, the IR spectra showed a relative increase in transmission at 1717 cm^{-1} corresponding to the loss of the carbamate carbonyl as it is converted to CO_2, compared to the nitrile stretch of the polymer matrix which changes minimally during the heating period.

The curing of epoxies is also known to produce a large DSC exotherm, specifically due to epoxide ring-opening by the amine. As shown by Figure 3, the cure exotherm only appears once the temperature of CO_2 release is reached. A subsequent DSC scan shows no further exotherm as the cure is complete. As shown in Table 1 for a variety of precursors, cure always follows deprotection, the onsets of which may differ by as little as 4 to as much as 16 °C. Interestingly, while the T_g values of the cured thermosets match well with those obtained from cured amine epoxies and depend upon the aliphatic or aromatic nature of the amine curing agent,[26] the measured enthalpy of cure is less than that typical of amine epoxies, generally regarded to be on the order of 100 kJ/equivalent of epoxide.[27]

When compared to the first entry in Table 1, a control system consisting of the byproducts of thermal carbamate deprotection, the lower energies of the bis-carbamate monomers are likely due to small amounts of evaporation of one or both byproducts during the release of CO_2. Because the carbamate deprotection follows Arrhenius kinetics, a statistical portion of the monomer will deprotect and thus cure at temperatures below the measured TGA onset. Isothermal DSC curing studies with precursors **13b** and **23**, the two lowest-curing monomers, reflect this behavior where both molecules can cure completely at 160 °C in ca. 90 and 50 min (Figure 4), despite having very similar deprotection onsets (170 and 176 °C, respectively).

Examination of the deprotection parameters for the various structures studied suggests the following: (i) 1,4--substitution leads to a lower deprotection temperature than 1,3,5-substitution, (ii) increasing the substitution of the benzylic carbon results in a lower deprotection temperature, and (iii) aryl bis-carbamates deprotect at lower temperatures than alkyl bis-carbamates. These patterns reflect an increase in the ability to stabilize a partial positive charge arising in the benzylic carbon in the transition

state and the well-known fact[15] that aryl carbamates are less thermally stable than their alkyl counterparts, presumably due to the electron-withdrawing effect of the aryl group.

As a result of curing, the gaseous carbon dioxide produced by the decomposition of the carbamate moieties remains trapped within the film forming spherical bubbles, shown by Figure 5. As expected, the size of these bubbles varies according to the curing temperature, with smaller bubbles formed within the film cured at a lower temperature, and dramatically larger bubbles formed in a film cured at a higher temperature. The size of the bubbles likely vary due to a variety of factors, most notably the impact of temperature on the rates of carbamate decomposition and curing. As the curing temperature increases, CO_2 is generated more quickly and is trapped to a larger extent within the rapidly curing film, resulting in larger bubbles. Lower curing temperatures both generate CO_2 more slowly and allow a greater amount of the generated gases to diffuse or escape from the film before it is fully cured.

In conclusion, we have developed a novel design strategy toward single component latent amine epoxies, in which we combine the latent amine and the epoxide onto the same molecule. The thermal trigger used in this epoxy design is analogous to that used for blocked isocyanates in polyurethane coatings. Utilizing a small library of epoxy precursors, we have shown that the cure temperatures can be adjusted through small structural changes to yield a range of self-curing epoxy-urethane monomers which cure in relatively short periods at elevated temperatures to give thermosets that may be useful as foam dielectrics, adhesives, sealants, and coatings.

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