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Development of a triazole-cure resin system for composites: Evaluation of alkyne curatives

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ABSTRACT

We are developing a resin system that cures via triazole ring formation (cycloaddition reaction of azides with terminal alkynes) instead of the traditional oxirane/amine reaction. The high exothermicity of the azido/alkyne reaction is expected to yield higher extents of reaction under ambient-cure conditions, making the resin system potentially suitable for "out-of-autoclave" curing processes. The difunctional azide-terminated resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A, was selected as the baseline diazide. A number of alkyne crosslinkers were synthesized and characterized, including propiolate esters of di- and trifunctional alcohols, propargyl esters of di- and trifunctional carboxylic acids, propargyl ethers of di- and trifunctional alcohols, and N,N,N′,N′-tetrapropargyl derivatives of primary diamines. Commercially available tripropargyl amine was also studied. Those systems employing a propiolate-based alkyne were found to be much more reactive toward the Huisgen 1,3-dipolar cycloaddition than the propargyl species. Curing energetics as a function of alkyne type, investigated through a dynamic differential scanning calorimetry approach, showed a distinct divide between the averaged activation energies of the propiolate and propargyl-type crosslinkers, 69.2–73.6 kJ/mol versus 82.3–86.4 kJ/mol, respectively. Cured network properties were readily manipulated through the incorporation of varying amounts of di- versus tri- and tetra-functional alkynes or through incorporation of soft alkylene and alkyleneoxy versus rigid aromatic polyalkynes. As expected, mechanical properties, e.g., the temperature of the tan δ peak in dynamic mechanical analysis, were found to increase with increasing crosslink density. These results have allowed us to select the most promising systems for scale-up and fabrication of samples of both pure resin and composites for traditional mechanical property testing, which will be reported in a subsequent paper.

1. Introduction

The use of advanced composite materials in high performance applications has been gaining popularity, due in part to their low weight and ability to withstand harsh loading conditions, e.g., those experienced in aerospace and marine applications. A significant challenge in designing these materials is the development of systems that can cure out-of-autoclave. In certain situations, the use of an autoclave is impossible, impractical, or uneconomical. Examples include the preparation of large composite panels encountered in marine applications and repair of existing composite panels incorporated into larger structures.

Curing of composite structures out-of-autoclave is facilitated by a chemistry that is highly exothermic. Thus, the crosslinking reaction can reach higher conversion prior to vitrification, without external heat [1]. Reaction between a terminal alkyne and an azide [2,3], the so-called Huisgen 1,3-dipolar cycloaddition reaction, is an excellent candidate for this application, and indeed, many attributes of the Huisgen reaction are expected to make it particularly advantageous toward the synthesis of advanced composite materials: it is easy to perform; it is tolerant to a wide range of impurities; it is high yielding; no small molecule is evolved, and most notably, the reaction is highly exothermic, with a ΔH between −210 kJ/mol and −270 kJ/mol [4]. The 1,2,3-triazole heterocycle formed during the cycloaddition has aromatic character, hydrogen bond accepting ability, and high chemical stability; it is largely inert to severe hydrolytic, oxidizing, and reducing conditions, even at high temperature [5].

It should be noted that while the Huisgen 1,3-dipolar cycloaddition is extremely exothermic, its activation energy is typically quite high, and triazole formation is often minimal at room temperature in the absence of catalyst. However, the reaction is

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exothermically autoaccelerating, whereby the heat generated by initial reaction events is sufficient to activate further reaction, in turn generating more heat; this is especially true for large reaction masses with low surface-to-volume ratios. For certain electrophilic alkynes, the activation barrier for reaction is relatively low, *ca.* 70 kJ/mol [6], and in such cases the reaction will occur at low temperatures, including room temperature, even without catalyst.

In several recent reports [6–9], we have described an azide-modified epoxy resin that cures via triazole ring formation, as opposed to the traditional oxirane/amine reaction (Fig. 1). This low temperature-cure composite matrix resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA), was first reported by Fokin, Finn, and coworkers [10] and is based on proven epoxy (epichlorohydrin/bisphenol-A) backbone chemistry. Kessler and coworkers have since also published on the subject [11]. In our work, commercially available epoxy resin (i.e., EPON 825) has been derivatized to carry azide end groups through a nucleophilic substitution reaction of the epoxide ring with NaN_3. The resulting liquid, azide-modified, epoxy resin may be cured with a variety of multifunctional alkynes representing a broad range of reactivities and chemical structures: propiolate vs. propargyl, aliphatic vs. aromatic, and di vs. tri- vs. tetra-functionality. Herein we explore these differences and how they affect the curing profiles and ultimate design of the resin system. Although these initial studies were conducted in the absence of catalyst, the effect of Cu(I) on the system will be the subject of subsequent reports. Additionally the fabrication of carbon filled composites utilizing a propargyl/DAHP-BPA resin system is currently being explored.

2. Experimental

2.1. Materials

All reagents were used without further purification. Tetra-*n*-butyl ammonium bromide (TBAB, 98%) was purchased from Fluka Chemicals. The diglycidyl ether of bisphenol-A (DGEBA, EPON 825) was donated by Hexion Specialty Chemicals. The remaining chemicals and all of the solvents were purchased from Sigma–Aldrich.

2.2. Instrumentation

Thermograms were recorded using a Q200 (TA Instruments) differential scanning calorimeter. The furnace atmosphere was defined by 50 mL/min of nitrogen. Polymer samples ranged from 5 to 12 mg and were analyzed in standard aluminum crucibles.

^{1}H and ^{13}C-NMR spectra were obtained using either a Varian Mercury 300 or a Varian UNITY-INOVA 500 MHz spectrometer with 5 mm o.d. tubes. Sample concentrations were approximately 25% (w/v) in either $CDCl_3$, CD_3CN, or DMSO-d_6 containing 1% TMS as an internal reference.

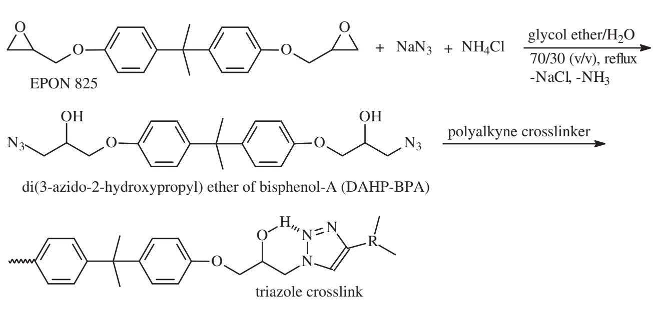

Fig. 1. Synthesis of azide-modified epoxy resin (DAHP-BPA) and its curing reaction with polyfunctional alkynes to form triazole crosslinks.

Dynamic mechanical analysis (DMA) was conducted using a Q800 (TA Instruments) instrument. The frequency was set at 1 Hz, the pre-load static force at 0.005 N, the oscillatory amplitude at 20 μm, and the track setting at 125%.

2.3. Synthesis of di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA)

To a 500 mL round-bottom flask equipped with a magnetic stir bar were charged 85.1 g DGEBA epoxy resin (EPON 825) (0.25 mol), 65.7 g ammonium chloride (1.23 mol), 64.3 g sodium azide (1.0 mol), 167 mL 2-ethoxyethanol (Cellosolve), and 83 mL deionized (DI) water. The reaction was allowed to stir until the majority of the reagents had dissolved. The reaction was then brought to reflux by submersing the flask into an oil bath at a constant temperature of 130 °C. The internal temperature of the reaction reached 107 °C; the pH remained in the neutral range, ca. 7–8. The reaction was allowed to reflux for 4 h with continuous stirring. The reaction contents were then cooled and added to a separatory funnel. To the funnel was added 250 mL DI water, and the mixture was extracted with ethyl acetate (2 × 250 mL). The organic layers were combined and washed with brine (2 × 250 mL) and DI water (2 × 250 mL), dried with $MgSO_4$, filtered, and vacuum stripped using a wiped film evaporator to yield the final product. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.63$ (s, 6H, CH_3), 2.55 (s, 2H, OH), 3.51 (m, 4H, CH_2–N_3), 3.99 (d, 4H, O–CH_2), 4.15 (m, 2H, C$\underline{H}$–OH), 6.82 (d, 4H, Ar–$C_{2,6}$-H), 7.12 (d, 4H, Ar–$C_{3,5}$–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.00$ (CH_3), 41.76 ($\underline{C}$–CH_3), 53.37 (CH_2–N_3), 68.97 (CH–OH), 69.33 (O–CH_2), 113.92 (Ar–$C_{3,5}$), 127.85 (Ar–$C_{2,6}$), 143.86 (Ar–C_1), 156.03 (Ar–C_4) ppm.

2.4. Synthesis of polyalkyne curing agents

The multifunctional alkyne curing agents used in this work are shown in Fig. 2. Tripropargyl amine (TPA) is commercially available and was obtained from Sigma–Aldrich. Syntheses for several of the propargyl and propiolate esters (DPA, TPTM, HDP, and TMPTP) were initially developed by Willer, Lin, and Baum at Fluorchem Inc., Azusa, CA, during development of triazole-cure propellants [12].

2.4.1. Synthesis of oligo(ethylene glycol) dipropiolates

A modification of the procedure of Miller [13] was used to synthesize three oligo(ethylene glycol) dipropiolates: poly(ethylene glycol)-200 dipropiolate (PEGDP), di(ethylene glycol) dipropiolate (DEGDP), and tetra(ethylene glycol) dipropiolate (TEGDP). The synthesis of tetra(ethylene glycol) dipropiolate is representative: tetraethylene glycol (77.6 g, 0.40 mol) was weighed into a dry 1000 mL round-bottom flask equipped with a magnetic stir bar, and dried by placing under high vacuum (<0.5 Torr) for 1 h at 60 °C. Propiolic acid (63 g, 95%, 0.85 mol), benzene (350 mL), and *p*-toluenesulfonic acid mono-hydrate (4.0 g) were added to the flask. A Dean–Stark trap and a condenser were attached, and the reaction was protected by a nitrogen bubbler. The mixture was heated at reflux for 20 h, and the water of condensation was separated (bath temp 110 °C). A total of 15.5 mL of water was collected (theory is 14.4 mL). The mixture was then cooled to below room temperature and transferred to a 1 L separatory funnel using two 200 mL diethyl ether rinses to insure complete transfer. The benzene-diethyl ether solution was washed with 20 wt% sodium hydroxide solution (1 × 25 mL). The solution was then washed with brine (1 × 25 mL), dried over $MgSO_4$, and filtered, and the solvent

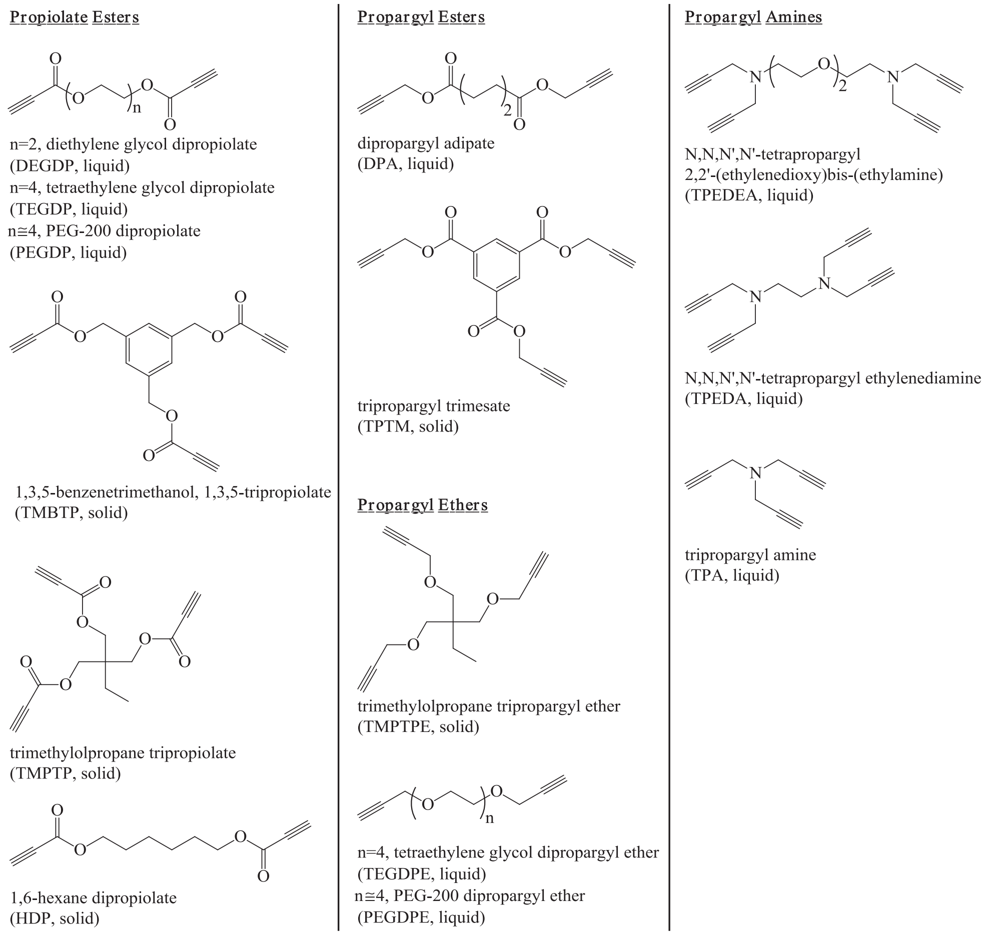

Fig. 2. Multi-functional alkyne curing agents used in this work: propiolate, propargyl esters, propargyl ethers, and propargyl amines.

was removed under reduced pressure. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 3.00$ (s, 2H, ≡C–H), 3.54 (s, 8H, CH$_2$–O), 4.25 (t, $J = 6.5$ Hz, 4H, $\underline{\mathrm{H}}_2$C–CH$_2$–O–CO), 4.31 (t, $J = 6.5$ Hz, 4H, CH$_2$–C$\underline{\mathrm{H}}_2$–O–CO) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 65.19$, 68.47, 70.53, 70.57 (CH$_2$–CH$_2$), 74.46 (C–$\underline{\mathrm{C}}$≡), 75.38 (≡C–H), 152.59(C═O) ppm.

2.4.2. Synthesis of 1,3,5-benzenetrimethanol, 1,3,5-tripropiolate (TMBTP)

First, 1,3,5-tri(hydroxymethyl)benzene was synthesized by the literature procedure developed by Moses [14]. The melting point of the product was 75–76 °C (lit. 75 °C [14]). Propiolic acid (2.45 g, 0.035 mol) was then weighed into a dry 100 mL round-bottom flask equipped with a magnetic stirring bar. Toluene (50 mL), 1,3,5-tri(hydroxymethyl)benzene (1.68 g, 0.010 mol), and *p*-toluenesulfonic acid mono-hydrate (0.2 g) were added to the flask. A Dean–Stark trap and a condenser were attached, and the reaction was protected by a nitrogen bubbler. The mixture was heated to reflux for 4.5 h, and 0.7 mL of water was separated (theory is 0.54 mL). Most of the water came off in the first hour. When the production of water ceased, the mixture was cooled to room temperature and transferred to a 250 mL separatory funnel. The toluene solution was washed with 5% sodium hydroxide solution (2 × 5 mL) and 10 mL of brine. It was then dried over MgSO$_4$ and filtered, and the solvent was removed under reduced pressure. The product slowly crystallized while under vacuum. The yield of crude product was essentially quantitative. A small sample was recrystallized from methanol to give crystals melting at 62–64 °C. FT-IR (film, warm): 3404(w), 3253(vs), 2951(m), 2892(m), 2119(vs), 1712(vs), 1461(m), 1370(m), 1241(vs), 1029(m), 966(m), 955(sh), 913(w), 867(m), 756(s), 710(m) cm^{-1}. ^{1}H NMR (DMSO-d$_6$): $\delta = 4.60$ (s, 3H, ≡C–H), 5.23 (s, 6H, CH$_2$–O), 7.41 (s, 3H, Ar–H) ppm. ^{13}C NMR (DMSO-d$_6$): $\delta = 67.35$ (CH$_2$–O), 74.96 (C–$\underline{\mathrm{C}}$≡), 79.95 (≡C–H), 128.89 (Ar–CH), 136.17 (Ar–C–), and 152.47 (C═O) ppm. HRMS (EI); C$_{18}$H$_{12}$O$_6$ [M]+: calcd. 324.0634; found 324.0635 amu.

2.4.3. Synthesis of trimethylolpropane tripropiolate (TMPTP)

Propiolic acid (70.05 g, 1.0 mol) was weighed into a dry 500 mL round-bottom flask equipped with a magnetic stirring bar. Toluene (250 mL), trimethylolpropane (40.25 g, 0.30 mol) and *p*-toluenesulfonic acid mono-hydrate (3.0 g) were added to the flask. A Dean–Stark trap and a condenser were attached, and the reaction was protected by a nitrogen bubbler. The mixture was heated to reflux for 4.5 h and 21 mL water was separated (theory is 16.2 mL). Most of the water came off in the first hour. The mixture was cooled to room temperature and transferred to a 1 L separatory funnel. Ethyl acetate (250 mL) was added to keep the product in solution. The toluene-ethyl acetate solution was washed with 5% sodium hydroxide solution (2 × 100 mL) and 100 mL of brine solution. It was then dried over MgSO$_4$ and filtered, and the solvents were removed under reduced pressure. The product slowly crystallized with a yield of 85.72 g (0.296 mol, 98.5%), and a melting point of 71–73 °C. The product contained traces of toluene, which were removed by melting the product and casting it into teflon pans as thin sheets and drying the sheets in a vacuum oven. An analytical sample was obtained by recrystallization from acetone, and it had a melting point of 80–82 °C. FT-IR (film, warm): 3283(m), 2973(w), 2121(s), 1717(vs), 1466(m), 1387(w), 1219(vs), 990(m), 752(m) cm^{-1}. ^{1}H NMR (DMSO-d$_6$): $\delta = 0.83$ (t, $J = 7.5$ Hz, 3H, $-CH_3$), 1.42 (q, $J = 7.5$ Hz, 2H, $\underline{C}H_2-CH_3$), 4.12 (s, 6H, CH_2-O), 4.58 (s, 3H, $\equiv C-H$) ppm. ^{13}C NMR (DMSO-d$_6$): $\delta = 7.51$ ($-CH_3$), 22.87 ($\underline{C}-(CH_2)_4$), 65.62 ($-CH_2$), 74.76 ($C-\underline{C}\equiv$), 80.08 ($\equiv C-H$), and 152.39 ($C=O$) ppm. Anal. calcd. for: $C_{15}H_{14}O_6$: C, 62.07; H, 4.86; Found: C, 62.27; H, 4.84%.

2.4.4. Synthesis of 1,6-hexane dipropiolate (HDP)

1,6-Hexane dipropiolate was prepared by the procedure of Wang et al. [15]. The melting point was 44–45 °C (lit. 42–45 °C [15]).

2.4.5. Synthesis of dipropargyl adipate (DPA)

Propargyl alcohol (12.0 g, 0.214 mol), pyridine (16.0 g, 0.202 mol), and dry dichloroethane (100 mL) were charged to a 500 mL round-bottom flask. The resulting solution was maintained at 10 °C by means of a salt/ice/water bath. A solution of adipoyl chloride (18.3 g, 0.10 mol) in 100 mL of dry dichloroethane was added dropwise over 15 min. The solution was stirred overnight at room temperature and then transferred to a 1 L separatory funnel with the aid of a small amount of dichloroethane. The dichloroethane solution was washed with water (2 × 100 mL), 5% HCl (100 mL), and saturated sodium bicarbonate solution (100 mL). The dichloroethane solution was dried over $MgSO_4$ and filtered, and the dichloroethane was removed under reduced pressure. The product was purified by vacuum distillation. The main fraction was collected at 0.7 Torr, boiling from 130 to 132 °C. The reported boiling point is 142–145 °C @ 4 Torr [16]. FT-IR (film): 3290(vs), 2947(s), 2874(m), 2129(m), 1740(vs), 1436(s), 1418(sh), 1382(s), 1350(sh), 1311(sh), 1235(s), 1164(s), 1077(m), 1027(m), 996(m), 959(m), 935(m), 680(s), 647(s) cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN): $\delta = 1.72$ (m, 4H, CH_2), 2.39 (m, 4H, CH_2-CO), 2.50 (t, 2H, $\equiv C-H$), 4.68 (d, 4H, $O-CH_2$) ppm. ^{13}C NMR (75 MHz, CD_3CN): $\delta = 24.04$ ($\underline{C}H_2-CH_2$-CO), 33.42 ($\underline{C}H_2-CO$), 51.82 ($O-CH_2$), 74.90 ($H-C\equiv$), 77.63 ($CH_2-\underline{C}\equiv$), 172.30 ($C=O$) ppm.

2.4.6. Synthesis of tripropargyl trimesate (TPTM)

Propargyl alcohol (18.0 g, 0.32 mol) and pyridine (24 g, 0.30 mol) were dissolved in 150 mL of anhydrous dichloroethane in a 500 mL round-bottom flask equipped with a magnetic stirring bar. This reaction was maintained at 10 °C by means of a salt/ice/water bath. A solution of trimesoyl chloride (26.6 g, 0.10 mol) in 100 mL of anhydrous dichloroethane was added drop-wise over 20 min. The solution was stirred overnight at room temperature. The next day the solution was transferred to a 1 L separatory funnel with the aid of a small amount of dichloroethane. The dichloroethane solution was washed with water (2 × 100 mL), 5% HCl (100 mL), and 5% sodium hydroxide solution (100 mL). The dichloroethane solution was then dried over $MgSO_4$ and filtered, and the dichloroethane was removed under reduced pressure. The product was purified by recrystallization from acetone. The yield was 29.16 g (0.09 mol, 90%). The melting point was 82 °C. FT-IR (film): 3296(vs), 3288(s), 3271(m), 3090(w), 2125(w), 1731(vs), 1609(w), 1445(s), 1433(w), 1375(s), 1364(m), 1329(s), 1277(sh), 1229(vs), 1151(m), 1103(m), 1022(s), 1001(s), 959(m), 930(m), 732(vs), 700(s), 684(s), 649(m) cm-1. cm^{-1}. ^{1}H NMR (DMSO-d$_6$) $\delta = 3.65$ (t, $J = 2.4$ Hz, 3H, $\equiv C-H$), 5.03 (d, $J = 2.4$ Hz, 6H, $O-CH_2$), 8.62 (s, 3H, Ar−CH) ppm. ^{13}C NMR (DMSO-d$_6$) $\delta = 51.84$ ($O-CH_2$), 74.90 ($H-C\equiv$), 77.64 ($CH_2-\underline{C}\equiv$), 124.05 (Ar−CH), 133.44 (Ar−C−), 172.33 ($C=O$) ppm. HRMS (EI); $C_{18}H_{12}O_6$ [M]+: calcd. 324.0634; found 324.0641.

2.4.7. Synthesis of trimethylolpropane tripropargyl ether (TMPTPE)

This compound was synthesized using a modification of the procedure of Mekni and Baklouti [17]. Trimethylolpropane (6.71 g, 0.050 mol) was weighed into a dry 100 mL round-bottom flask equipped with a mechanical stirrer, condenser, and septum. Sodium hydroxide (12 g, 0.30 mol), water (1.0 mL), and TBAB (0.80 g) were added, and the temperature of the solution was adjusted to 25 °C. The reaction was protected by a nitrogen bubbler. Propargyl bromide (45.0 g of 80 wt% solution in toluene, 0.30 mol) was added drop-wise over the course of 1 h, and then the temperature was slowly raised to 60 °C over the course of 1 h. During this time the reaction became homogeneous. The reaction mixture was stirred at 60 °C overnight. It was then cooled and diluted with 100 mL of methylene chloride and filtered to remove salts. The salts were extracted with two 100 mL portions of methylene chloride, and the extracts were filtered and combined with the main reaction. The crude product was observed to be contaminated with some very fine salts that went through the filter. The solvents were stripped, and the crude product (yield = 15.01 g) was analyzed by ^{1}H NMR. Except for small amounts of toluene and propargyl bromide, the product was quite pure. The remaining toluene and propargyl bromide were removed under high vacuum, and the product was distilled using a Kugelrohr apparatus (200 °C @ 0.40 Torr), to yield 10.5 g (42.3 mmol, 84.6%) of purified product. NMR analysis indicated that the purified product was 90% tri- and 10% dipropargylated. ^{1}H and ^{13}C-NMR chemical shifts were in excellent agreement with reported values [18]. FT-IR (film): 3294(vs), 2880–3000(b, vs), 2117(m), 1721(w), 1475(s), 1442(m), 1360(s), 1265(m), 1084(s), 1025(m), 975(m), 912(m) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, 3H, $J = 4.2$ Hz, $-CH_3$), 1.42 (q, 2H, $J = 4.2$ Hz, $\underline{C}H_2-CH_3$), 2.42 (t, 3H, $J = 2.4$ Hz, $\equiv C-H$), 3.40 (s, 6H, CH_2-O), 4.14 (d, 6H, $J = 2.4$ Hz, $O-CH_2-C\equiv$) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 7.42$ ($-CH_3$), 22.62 ($\underline{C}H_2-CH_3$), 42.66 ($\underline{C}-(CH_2)_4$), 58.48 ($O-\underline{C}H_2-C\equiv$), 70.12 ($O-\underline{C}H_2-C$), 74.19 ($H-C\equiv$), 80.09 ($C-\underline{C}\equiv$) ppm.

2.4.8. Synthesis of oligo(ethylene glycol) dipropargyl ethers

Two compounds, tetra(ethylene glycol) dipropargyl ether (TEGDPE) and poly(ethylene glycol)-200 dipropargyl ether (PEGDPE), were made using a modification of the procedure of Mekni and Baklouti [17]. The synthesis of tetra(ethylene glycol) dipropargyl ether is representative: tetraethylene glycol (19.4 g, 0.10 mol) was weighed into a dry 250 mL three-neck round-bottom flask equipped with a mechanical stirrer, septum, and a condenser. Sodium hydroxide (16.0 g, 0.40 mol), water (2 mL), and TBAB (0.40 g) were added to the flask, and the reaction was protected by a nitrogen bubbler. The mixture was heated to 45 °C, and propargyl bromide (60 g of 80 wt% solution in toluene, 0.40 mol) was added drop-wise over 1 h. Following addition, the reaction temperature was raised to 60 °C and stirred for 6 h. The mixture was cooled and diluted with 100 mL of methylene chloride. The mixture was filtered to remove salts; the salts were extracted with methylene chloride (2 × 50 mL), and the combined solutions were stripped of solvents. FT-IR spectroscopy showed that no hydroxyl remained, indicating reaction completion. The yield of crude product was 32.28 g. The remaining toluene and propargyl bromide were removed under high vacuum, and the resulting product was Kugelrohr distilled at 200 °C @ 0.50 Torr in two batches. The reported boiling point was 110 °C @ 0.1 Torr [17]. The yield of purified product was 26.46 g (98 mmol, 98%). FT-IR (film): 3251(m), 2870(s), 2113(w), 1458(w), 1350(m), 1270(w), 1250(w), 1102(vs), 1033(m), 919(w), 842(w) cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN): $\delta = 4.16$ (d, $J = 2.4$ Hz, 4H, $O-CH_2-C\equiv$), 3.60 (s, 8H), 3.40 (s, 8H), 2.74 (t, $J = 2.4$ Hz, 2H, $H-C\equiv$) ppm. ^{13}C NMR (75 MHz, CD_3CN): $\delta = 57.82$, 69.05, 70.02, 70.02, 70.25 ($O-\underline{C}H_2-C\equiv$), 74.94 ($H-C\equiv$), 80.08 ($C-\underline{C}\equiv$) ppm.

2.4.9. Synthesis of N,N,N′,N′-tetrapropargyl-2,2′-(ethylenedioxy) bis(ethylamine) (TPEDEA)

To a 3-neck 500 mL round-bottom flask, equipped with a mechanical stirrer, were charged 2,2′-(ethylenedioxy) bis(ethylamine) (14.82 g, 0.10 mol), water (40 mL), sodium hydroxide (17.6 g, 0.44 mol), dichloroethane (80 mL) and TBAB (0.322 g). A reflux condenser equipped with a nitrogen bubbler was attached, and a room temperature bath was placed around the flask. Propargyl bromide (65.46 g of 80 wt% solution in toluene, 0.44 mol) was added drop-wise over the course of 1 h, and the mixture was stirred overnight. The mixture was transferred to a 1 L separatory funnel with the aid of 400 mL of methylene chloride. The pH of the aqueous layer was checked and found to be slightly basic. The aqueous layer was separated, and the organic layer was dried over magnesium sulfate, filtered, and then solvent-stripped to yield the crude product (32.5 g). The crude product was chromatographed on 250 g of silica using an 80/20 solution of methylene chloride/ethyl acetate as the eluent; 150 mL fractions were collected. A very dark band eluted as fraction 3, with fractions 5–8 containing the desired compound. These fractions were combined and solvent-stripped to give 17 g (57 mmol, 57%) of a slightly yellow-brown product. Thin layer chromatography (TLC) showed that fractions 9 and 10 might also contain the desired compound. They were combined and solvent-stripped, yielding an additional 3.1 g (10 mmol, 10%). NMR analysis showed both products were the desired tetra-functional compound. FT-IR (film) = 3300 (vs), 2924(m), 2821(m), 2103(w), 1672(w), 1642(w), 1440(m), 1352(m), 1328(m), 1124(m), 1101(m), 1055(w), 977(w), 902(m), 832(w), 806(w), 636(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.45 (t, J = 2.4 Hz, 4H, $\underline{H}-C\equiv$), 2.68 (t, J = 7 Hz, $NC\underline{H}_2-CH_2O$), 3.45 (d, J = 2.4 Hz, 8H, $N-CH_2-C\equiv$), 3.55 (s, 4H, $OC\underline{H}_2CH_2O$), 3.60 (t, J = 7 Hz, 4H, $NCH_2-C\underline{H}_2O$) ppm. ^{13}C NMR (CD_3CN): δ = 42.46 ($N-\underline{C}H_2-C\equiv$), 52.40 ($N-\underline{C}H_2-CH_2$), 69.51 ($O-CH_2CH_2$), 70.32 ($O-\underline{C}H_2CH_2$), 73.73 ($H-\underline{C}\equiv$), 79.41 ($C-\underline{C}\equiv$) ppm. HRMS (NCI): $C_{18}H_{25}N_2O_2$ $[MH]^+$: calc. 301.1916; found 301.1904 amu.

2.4.10. Synthesis of N,N,N′,N′-tetrapropargylethylenediamine (TPEDA)

This compound was prepared using a modification of the procedure of Yamada and Aoki [19]. To a 3-neck 500 mL round-bottom flask, equipped with a mechanical stirrer, were charged ethylene diamine (6.0 g, 0.10 mol), water (40 mL), sodium hydroxide (17.6 g, 0.44 mol), dichloroethane (80 mL), and TBAB (0.322 g). A reflux condenser equipped with a nitrogen bubbler was attached, and a room temperature bath was placed around the flask. Propargyl bromide (65.46 g of 80 wt% solution in toluene, 0.44 mol) was then added drop-wise over 1 h, and the reaction was stirred for 22 h at room temperature. The mixture was then transferred to a 500 mL separatory funnel with the aid of 100 mL of dichloroethane and 100 mL of water. The pH of the aqueous layer was checked to ensure it was basic. A very stable emulsion formed; so the mixture was filtered through a fiberglass filter to remove any polymeric impurities before returning it to the separatory funnel. The organic layer was separated, dried over magnesium sulfate, filtered, and then solvent-stripped to give the crude product (28.2 g). TLC showed at least three products. The crude product was chromatographed on 200 g of silica using methylene chloride as the eluent, collecting 150 mL fractions. A very dark band eluted at fractions 3 and 4 and contained a solid material, perhaps a quaternary salt. Fractions 6–11 contained the desired crude compound (8.5 g). Fractions 6–11 were combined, solvent-stripped, and Kugelrohr distilled (175 °C @ 0.5 Torr) to give 5.9 g (28 mmol, 28%) of slightly yellow product. FT-IR (film) = 3292(vs), 2900(m), 2870(s), 2821(m), 2375(w), 2344(w), 2103(w), 1734(w), 1442(m), 1352(m), 1328(m), 1247(m), 1117(m), 902(m), 839(w), 802(w), 635(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.21 (t, J = 2.4 Hz, 4H, $\underline{H}-C\equiv$), 2.68 (s, 4H, $C\underline{H}_2-C\underline{H}_2$), 3.45 (d, J = 2.4 Hz, 8H, $N-CH_2-C\equiv$) ppm. ^{13}C NMR ($CDCl_3$): δ = 42.47 ($\underline{C}H_2-\underline{C}H_2$), 49.89 ($N-\underline{C}H_2-C\equiv$), 73.19 ($H-\underline{C}\equiv$), 78.66 ($C-\underline{C}\equiv$) ppm. HRMS (CI): $C_{14}H_{17}N_2$ $[MH]^+$: calc. 213.1392; found 213.1383 amu.

2.5. Neat linear polymerization

Neat, linear polymerizations were conducted by combining difunctional alkynes DEGDP and DPA with DAHP-BPA such that the molar ratio of azide:alkyne was 1:1. A high density polyethylene scintillation vial (20 mL) served as the polymerization reactor. A mixture of two alkyne monomers was used to create three different curing conditions: A) 50/50 DEGDP/DPA, cured at 100 °C for 2 h, B) 50/50 DEGDP/DPA, cured at RT for 12 h, then at 100 °C for 2 h, and C) 65/35 DEGDP/DPA, cured at 100 °C for 2 h. All systems were mixed for 5 min, and then 0.5 g of the mixture was charged to a vial. The polymerization conditions were chosen to limit molecular weight and maintain solubility of the product in common solvents.

2.6. Differential scanning calorimetry sample preparation

Differential scanning calorimetry (DSC) samples were prepared by combining azide-modified epoxy resin DAHP-BPA and polyalkyne crosslinker(s) such that the ratio of azide to alkyne functionality was 1:1 and the total reaction mass was approximately 0.3 g. When a combination of a solid and a liquid alkyne component was used, prior to combining with DAHP-BPA, the solid alkyne component was dissolved in the liquid alkyne component by warming the mixture. Alkyne and azide components were then combined and mixed for 5 min, after which 5–12 mg of the mixture was charged to a standard, capped aluminum DSC pan. Once the pans were prepared either a DSC run was immediately conducted or the sample was placed in the freezer until DSC was conducted. Those samples placed in the freezer were run within 12 h.

The ASTM E698 method [20] was applied to DAHP-BPA resin/alkyne crosslinker formulations derived from all eleven alkyne crosslinker types shown in Fig. 2. Each sample was equilibrated in the DSC for 2 min at 0 °C and then heated to 300 °C at a predetermined heating rate, β. Each formulation was analyzed at five heating rates (β = 2, 5, 10, 15, and 20 °C/min), and each formulation/heating rate combination was analyzed in duplicate. A follow-up dynamic scan was conducted at 10 °C/min to ensure that there was no residual exotherm and that the curing reaction had gone to completion. The maximum exotherm temperature, $T_{\max}$, was determined for each run from curves similar to those in Fig. 3. Linear plots of ln (β) versus ($T_{\max}^{-1}$) were then constructed and used to calculate E_a from the slope.

2.7. Rheological sample preparation

Viscosity of developing networks was measured using an ARES (TA Instruments) Rheometer. All tests were conducted at room temperature and at a frequency of 1 Hz. Uncured resin systems were mixed according to the above DSC specifications and carefully poured onto parallel 25 mm aluminum plates.

3. Results and discussion

3.1. Synthesis of di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA)

Sharpless and coworkers first reported the synthesis of DAHP-BPA in 2007 [10]. The structure of their product was identical to that shown in Fig. 1 (attack of azide ion on the less substituted carbon of the epoxide ring). They reported the use of $NaN_3/LiClO_4$ in acetonitrile at 90 °C overnight, followed by the addition of water,

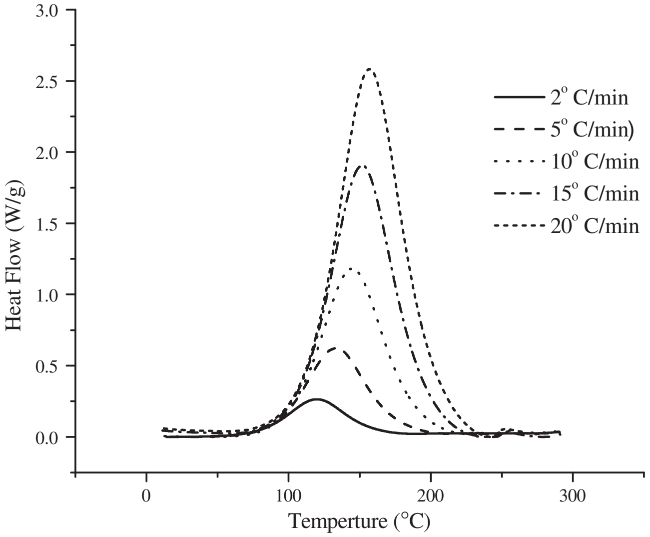

Fig. 3. Dynamic DSC curves for the DAHP-BPA/TEGDPE system at heating rates of 2, 5, 10, 15, and 20 °C (exothermal direction up). The exotherm temperature maxima, T_{max}, and ΔH were determined.

and extraction of the product into ethyl acetate. The extraction was washed with water and the product isolated by the removal of the solvent. We used a modification of this procedure in which the acetonitrile was replaced with a mixture of 2-ethoxyethanol (Cellosolve) and water (3:1, v/v), with NH_4Cl charged to the reaction at the beginning to serve as a proton source and to help catalyze the epoxy ring opening [21]. The pH was monitored over the course of the reaction to ensure it remained in a neutral range, ca. 6–9; typically, no adjustment was necessary. When outside this pH range the reaction has been reported to become sluggish [22]. Use of 2-ethoxyethanol enabled a higher reaction temperature (107 °C), and this modification, coupled with the addition of ammonium chloride, lead to an increase in reaction rate. These conditions produced complete reaction in about 4 h, yielding a single product with ^{1}H and ^{13}C-NMR chemical shifts identical to those reported by Sharpless et al. [10]. This procedure was also successfully scaled to produce 2 kg of DAHP-BPA in a single reaction.

More recently Kessler and coworkers reported the synthesis of DAHP-BPA by reaction of EPON 828 with NaN_3/NH_4Cl for 12 h in refluxing methanol [11]. However, these authors reported that the azide group was substituted at C2 of the glycidyl group (attack of azide ion on the more substituted carbon of the epoxide ring) and that two diasteromers were obtained (major and minor). Whether Kessler et al. obtained a different regioisomer is questionable since the chemical shifts they reported for their major isomer are identical to those observed by us and reported by Sharpless et al. Both DAHP-BPA and the EPON reactant should consist of two diastereomers, i.e., a pair of enantiomers and a meso compound, but the ratio should be 50:50. We observed only one set of peaks in the ^{13}C-NMR spectrum, suggesting that the chemical shift differences between diastereomers are vanishingly small.

3.2. *Synthesis of alkyne crosslinkers*

Two basic building blocks were employed to create polyfunctional alkyne crosslinkers: propioloyl and propargyl. A number of the alkyne species have been previously described in literature, and were synthesized by applying modifications to these methods [13,15,17,19]. Two alkyne compounds are novel and previously undescribed: TPEDEA and TMBTP. The propiolate esters were the first class of alkynes species to be synthesized, followed by the propargyl esters, and then the propargyl ethers and amines. As a general summary, the propiolate esters were readily synthesized by condensing the appropriate polyol with a slight excess of propiolic acid in refluxing toluene and in the presence of a catalytic amount of *p*-toluenesulfonic acid. The propargyl esters were synthesized by the reaction of the appropriate acid chloride with a slight excess of propargyl alcohol in toluene or dichloroethane using one equivalent of pyridine as an acid acceptor. The propargyl ethers were synthesized by reaction of the corresponding polyol with a large (2X) excess of propargyl bromide under forcing phase-transfer conditions. And finally, the propargyl amines were synthesized by reaction of the corresponding amine with only a slight excess of propargyl bromide to avoid formation of quaternary salts.

Crosslinkers that are solid at room temperature proved troublesome to mix with the azide-modified epoxy resin, yielding formulated resins with higher that optimal viscosity for fabrication of composite materials. Furthermore, the susceptibility to hydrolytic degradation of the ester linkage found in the propiolates and propargyl esters was of some concern. All of the propargyl ether and propargyl amine compounds have proven to be liquids, circumventing both issues. The propargyl amines have the added advantage of high functionality and low equivalent weight, thus offering a low-viscosity curative with the potential for higher crosslink density in the final thermoset, and making them excellent candidates for scale-up and fabrication of both pure resin and composite samples. Among the amines, TPA has the additional advantage of commercial availability.

3.3. *Linear polymerizations*

The reaction between azide-modified epoxy resin and the alkyne curatives was initially investigated using difunctional alkynes, which yielded linear polymer products. In this initial study, a mildly elevated curing temperature of 100 °C was employed. Although room temperature-cure remained the ultimate goal of the project, here we wanted to ensure that the monomers would in fact polymerize, and the use of elevated cure temperatures was the easiest pathway to that information. Mixtures of two alkyne monomers, DEGDP and DPA, were used to create three different resin systems, all at a theoretical 1:1 azide:alkyne stoichiometric ratio. Molecular weight was limited by controlling the time held at 100 °C, i.e., by limiting conversion, in order to maintain solubility in common GPC solvents. Fig. 4 shows gel permeation chromatograms of the starting epoxy resin, the azide-modified resin, and the chain-extended polymers. The chromatograms show that the addition of azide to the epoxy resin results in a significant increase in hydrodynamic volume, while the peak shape remains the same, indicating the lack of degradation, fractionation, or chain coupling/extension during reaction with the azide. Upon polymerization the peaks shift to shorter elution times, and broaden, clearly indicating an increase in molecular weight. Table 1 lists the quantitative results obtained from GPC-MALLS. Average degree of polymerization, $\overline{X}_n$, was calculated as number average molecular weight, $\overline{M}_n$, obtained from MALLS, divided by the average molecular weight of the structural units in the polymer (assuming that the propiolate and propargyl ester monomers entered the polymer in proportion to their relative abundances in the feed). The greatest $\overline{X}_n$ was obtained for the system containing the higher proportion (65 mol%) of the more reactive propiolate monomer. The two systems formulated at equimolar ratio of propiolate/propargyl produced the same $\overline{X}_n$, but the sample immediately reacted at 100 °C produced a narrower distribution of degrees of polymerization. Triazole formation was confirmed by ^{1}H NMR analysis; Fig. 5 shows

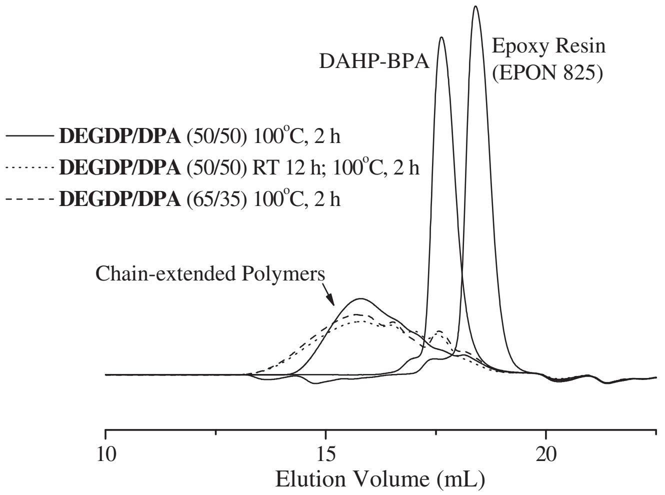

Fig. 4. GPC chromatograms (differential refractometer) of epoxy resin (EPON 825), DAHP-BPA, and three linear polytriazoles obtained by the reaction of DAHP-BPA with a mixture of DEGDP and DPA.

a representative spectrum. The proton resonances associated with the triazole rings are clearly visible at 8.69 and 8.27 ppm for the propiolate-based triazoles, and at 8.04 and 7.68 ppm for the propargyl-based triazoles. The triazole protons of the 1,4-regioisomers appear downfield relative to those of the 1,5-regioisomers. For both the propiolate- and propargyl-based triazoles, the 1,4-regioisomer was the major product.

In Fig. 6, dynamic DSC scans, conducted at a scan rate of 10 °C/min, compare the curing rate of azide-modified epoxy resin with a representative alkyne of each type: TMBTP (propiolate ester type), TPTM (propargyl ester type), TMPTPE (propargyl ether type), and TPA (propargyl amine type), as well as a commercial aerospace resin system composed of EPON 825 and an amine crosslinker, 4,4′-diaminodiphenyl sulfone (4,4′-DDS). The significantly higher reactivity of the propiolate type, as compared to the propargyl and the EPON 825/4,4′-DDS system, is evident from the earlier (lower temperature) onset of the exothermic curing reaction. The initial propiolate ester exotherm occurred at a relatively low temperature of ca. 18 °C. In comparison, the three propargyl-based crosslinkers showed much lower reactivity and did not begin to exotherm until 75 °C, while the EPON 825/4,4′-DDS system did not begin to exotherm until 150 °C. The low temperature reaction onset of a propiolate could be used to kick start the reaction of a propargyl species when the two monomers are used in tandem. For all azide/alkyne polymerizations, the total heat of reaction was approximately the same, ca. 700 J/g.

A systematic study was conducted to compare formulations containing varying amounts of propiolate and propargyl species, specifically HDP and DPA. These two alkynes were chosen because they have equivalent molecular weights. The samples were studied by dynamic DSC and through rheological measurements (Figs. 7 and 8). A total of 7 systems were investigated, containing relative ratios of DPA/HDP of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100, respectively. All systems were formulated so that the molar ratio of total azide to total alkyne was 1:1. The DSC peak exotherm shifted from ca. 138 °C for the system containing 100% DPA to ca. 89 °C for the system containing 100% HDP; all systems containing a mixture of the two alkyne species displayed a bimodal thermogram. In addition to the two exotherms observed at ca. 89 °C and 138 °C, a third exotherm was observed ca. 250 °C for those systems incorporating the HDP alkyne. The size of the exotherm at 250 °C increased as the HDA content increased, and was not observed in the system containing 100% DPA, indicating that the HDA cures by a more complex mechanism. Overall, we observed that a very high rate of heat release can result in uncontrollable reactions, as seen in some propiolate systems. The bimodal curing profiles displayed by the DPA/HDP mixtures offer a potential solution to this problem by releasing the heat in two fractions.

The same DPA/HDP blends were reacted with DAHP-BPA isothermally at room temperature and viscosity was monitored as a function of time (Fig. 8). For the system containing 100% DPA, viscosity was found to remain relatively constant over the course of the experiment, with no appreciable increase. This indicated that resin compositions consisting of DAHP-BPA and propargyl-type alkynes are shelf-stable for long periods (days) in the absence of catalyst. In comparison, the system utilizing 100% HDP was found to vitrify after ca. 600 min. The rheological profiles of those systems containing a mixture of DPA and HDP fell between these two extremes, predictably in accordance with the propiolate/propargyl ratio. Triazole formation at room temperature was confirmed by ^{1}H NMR analysis for the systems composed of 100% HDP and the 20/80 DPA/HDP system. Samples were mixed according to the standard procedure and were allowed to react at room temperature for 24 h. Fig. 9 shows ^{1}H NMR spectra for the resulting polytriazoles, where the chemical shifts associated with the propiolate triazole proton, for the 1,4- and 1,5-regioisomer, were found at 8.69 and 8.27 ppm, respectively. For the 20/80 DPA/HDP system, the spectrum was dominated by the propiolate triazole protons, and no peaks associated with the propargyl triazole were detected, which are predicted to occur at 8.04 and 7.68 ppm. This was expected since the propiolate is much more reactive than the propargyl species.

We concluded our studies of relative reactivity by determining the averaged activation energy, E_a, of our polyalkyne crosslinkers in the absence of catalyst, using the ASTM E698 method [20] (Table 2). This method is based on the variable program rate method of Ozawa, which requires three or more experiments at different heating rates, typically between 1 and 20 °C/min. The Ozawa approach assumes Arrhenius behavior, and that the extent of reaction at the peak exotherm is constant and independent of heating rate. In combination with Doyle's approximation [23], this approach yields the following equation:

$$\ln(\beta) = A' - \frac{1.052\, E_a}{RT_{\max}}$$

Table 1
GPC results comparing linear polymerization to the modified and unmodified resins.

	$\overline{M}_n$[a] (g/mol)	$\overline{M}_w$[a] (g/mol)	PDI	Theor. $\overline{M}_n$ (g/mol)	$\overline{X}_n$
EPON 825	340	350	1.03	340.41	–
DAHP-BPA	450	460	1.02	426.47	–
Diethylene glycol dipropiolate (DEGDP)	–	–	–	210.18	–
Dipropargyl adipate (DPA)	–	–	–	222.24	–
DEGDP/DPA (50/50) 100 °C, 2 h	2830	4390	1.55	–	8.8
DEGDP/DPA (50/50), RT 12 h, 100 °C 2 h	2900	6100	2.11	–	9.0
DEGDP/DPA (65/35) 100 °C 2 h	3720	6730	1.81	–	11.6

[a] GPC-MALLS.

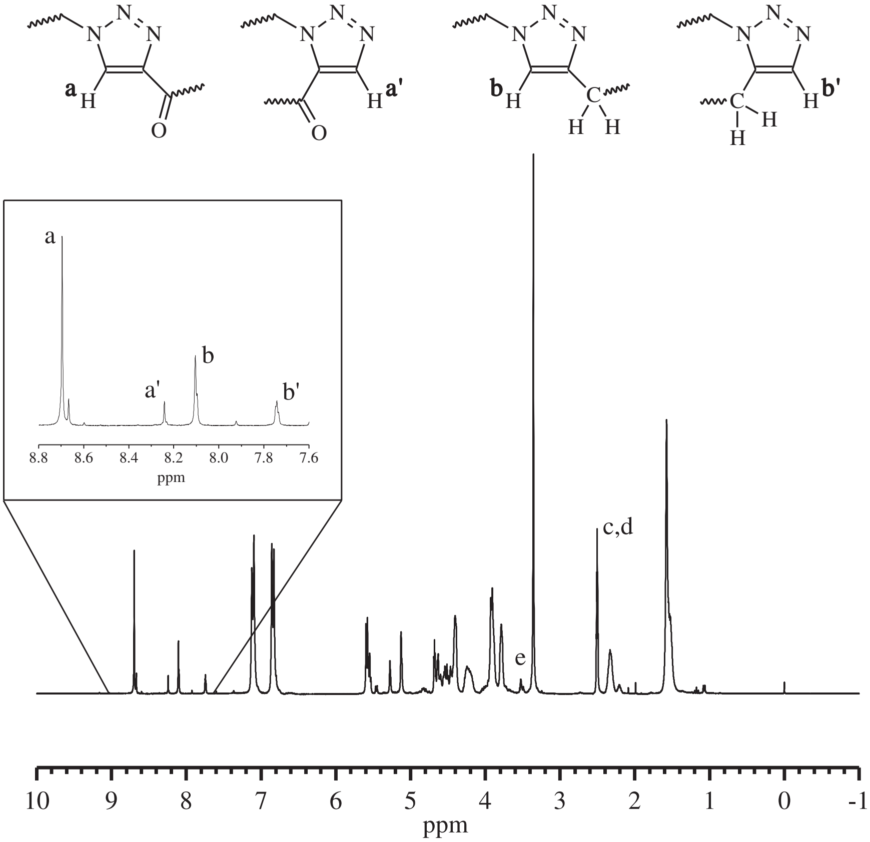

Fig. 5. ^{1}H NMR spectrum (d$_6$-DMSO, 23 °C) of a representative linear polytriazole from bulk polymerization of DAHP-BPA with 50/50 DEGDP/DPA conducted at 100 °C for 2 h. The triazole protons associated with the 1,4- and the 1,5-regioisomer, for the propiolate and propargyl linkages, have been denoted (a) and (a′) and (b) and (b′), respectively.

where β is the scan rate (K/min), A' is a constant, E_a is activation energy (J/mol), T_{max} is the temperature at maximum exotherm (K), and R is the universal gas constant (8.314 J/mol K). Activation energy E_α can be calculated from the slope of linear plots of ln(β) versus 1/T_{max}. Typical dynamic DSC curves at a range of heating rates of 2, 5, 10, 15, and 20 °C/min are shown in Fig. 3, and it can be seen that peak temperature, T_{max}, shifts to higher temperatures as the heating rate, β, is increased. For all samples the linear fit coefficient of determination (R^2) was greater than 0.99. Furthermore, from the follow-up scan, all systems had gone to completion, as evidenced by the absence of any residual exotherm.

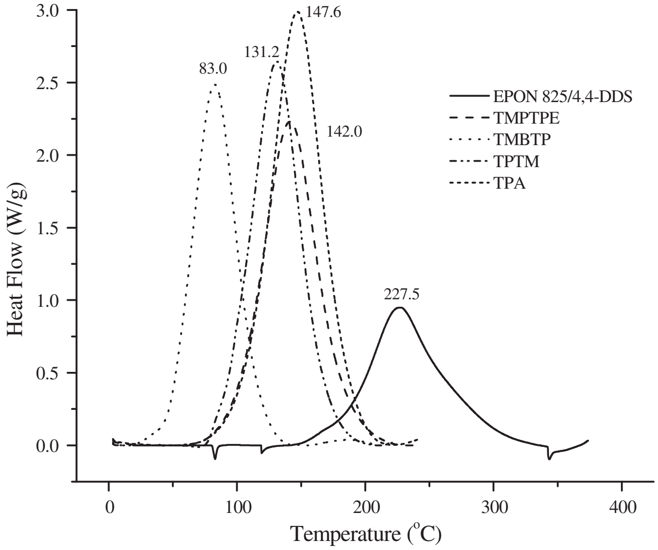

Fig. 6. Dynamic DSC scans obtained at 10 °C/min (exothermal direction up), comparing the curing rates of DAHP-BPA with a representative from each class of alkyne species: TMBTP (propiolate ester), TPTM (propargyl ester), TMPTPE (propargyl ether), and TPA (propargyl amine).

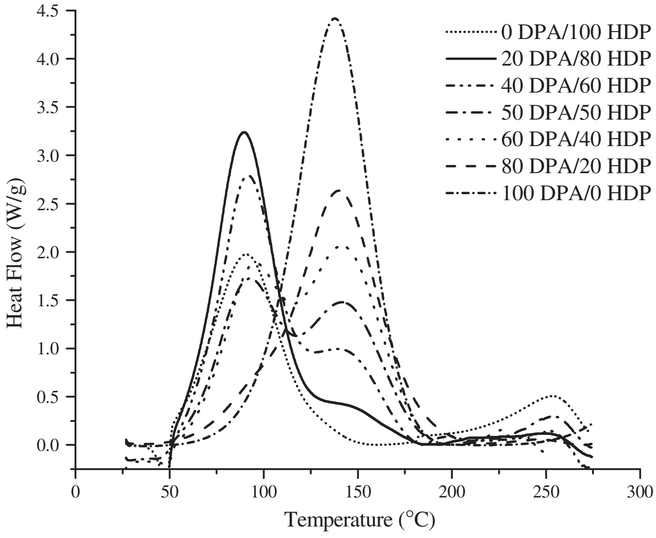

Fig. 7. Dynamic DSC scans obtained at 10 °C/min (exothermal direction up), comparing the curing rates of DAHP-BPA with various blends of DPA and HDP, ranging from 100% DPA to 100% HDP.

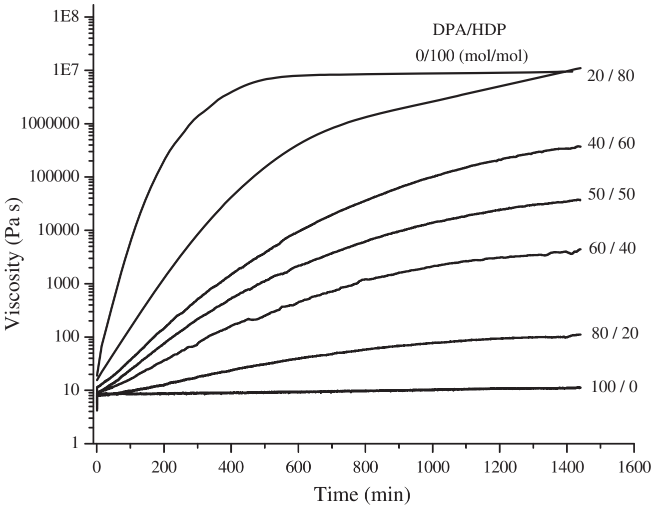

Fig. 8. Viscosity vs. time for mixtures of DAHP-BPA with various DPA/HDP blends, ranging from 100% DPA content to 100% HDP. Data were collected at 1 Hz and room temperature.

As expected, a propiolate compound, TMBTP, was determined to have the lowest averaged E_a (69.2 kJ/mol) of all crosslinkers studied. Furthermore all propiolate-based crosslinkers displayed approximately the same averaged E_a, with values ranging from 69.2 to 73.6 kJ/mol. In contrast, TPTM crosslinker, a propargyl type, displayed the highest averaged E_a, 86.4 kJ/mol. All of the propargyl-type structures displayed relatively high values ranging from 82.3 to 86.4 kJ/mol. Although a distinct divide was evident between the propiolate and propargyl crosslinkers, no significant difference in E_a was observed among the propargyl ether, propargyl amine, and propargyl ester subdivisions.

The normalized enthalpy of reaction, ΔH, was also determined for all systems by integration of the dynamic DSC peaks for each scan rate. The ΔH values ranged from −200 to −264 kJ/mol. Determination of ΔH suffers from higher error, due in part to baseline selection and baseline irregularities, as compared to T_{max} which is not significantly affected by baseline shifts. In general the determined ΔH were within the predicted ΔH range for the Huisgen 1,3-dipolar cycloaddition, −210 and −270 kJ/mol. These numbers indicate that the Huisgen reaction is extremely exothermic among organic reactions generally.

The highly exothermic nature of the Huisgen cycloaddition represents an opportunity in terms of out-of-autoclave curing but also a significant challenge. Too rapid heat release during cure can lead to burning and decomposition of the network. The reported heat capacity of epoxy resins is in the range 1.3–2.1 J/g-K [24]. Assuming that the heat capacity of our resin is similar (for example, 1.6 J/g-K), then the DAHP-BPA/TPA system at 1:1 stoichiometry would have a heat capacity of about 411 J/mol-K, and therefore, a reaction exotherm of about 130 kJ/mol would be sufficient to bring the system from room temperature to the decomposition temperature of 340 °C [25] under adiabatic conditions. This clearly shows that the total heat of reaction from the Huisgen cycloaddition is more than sufficient to cause severe decomposition of the reacting mass, at a typical equivalent weight used herein. Therefore, the rate of reaction must be carefully balanced with the rate of heat loss, which is dependent on section thickness of the reacting mass, heat conductivity of the surroundings, etc. Fortunately, rate of reaction can be controlled by alkyne choice and catalyst, and in fact, the bimodal curing profiles displayed by the propargyl/propiolate mixtures offer the flexibility of releasing the heat in multiple stages.

3.3.1. Crosslink density

In addition to reactivity, crosslink density and resulting physical properties can be manipulated though selective blending of different alkyne types; in particular, glass transition temperature of the resulting network can be strongly affected by incorporation of linear polyethylene glycol based alkyne species. Fig. 10 displays plots of tan δ versus temperature, obtained by DMA, of DAHP-BPA cured with various mixtures of PEGDP and TMPTP. A total of 5 systems were investigated, containing relative ratios of PEGDP/TMPTP of 100/0, 80/20, 70/30, 60/40, and 50/50. The systems were stirred for 5 min, molded, and allowed to react at 70 °C for 2 h. All systems were formulated so that the molar ratio of total azide to total alkyne was 1:1. For each curve, the peak maximum represents the glass transition temperature of the cured resin at that particular

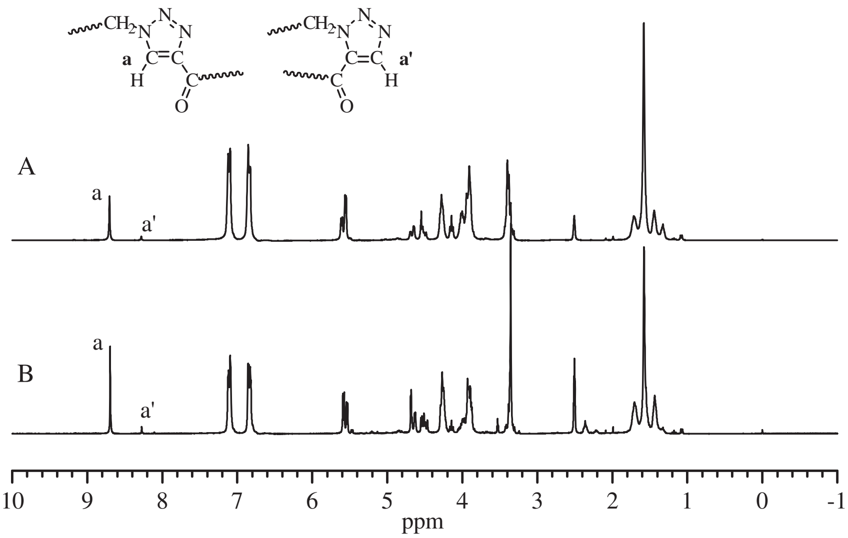

Fig. 9. ^{1}H NMR spectra (d$_6$-DMSO, 23 °C) of polytriazoles from bulk polymerization of DAHP-BPA with (A) 0/100 DPA/HDP, and (B) 20/80 DPA/HDP. Polymerizations were conducted at room temperature for 24 h with a theoretical 1:1 azide:alkyne stoichiometric ratio. The triazole protons associated with the 1,4- and the 1,5-regioisomer, for the propiolate linkage, have been denoted (a) and (a'), respectively.

Table 2
Activation energies and other kinetic parameters by the ASTM E698 method for the reaction of DAHP-BPA with the indicated alkyne.

	Alkyne	E_a (kJ/mol)	Avg ΔH (J/g)	Avg ΔH (kJ/mol)
Propiolate	TMBTP	69.2	−660 ± 60	−210 ± 19
	HDP	70.0	−600 ± 50	−200 ± 17
	TEGDP	72.3	−651 ± 8	−236 ± 03
	TMPTP	73.6	−850 ± 10	−264 ± 03
Propargyl	DPA	82.3	−780 ± 20	−242 ± 06
	TMPTPE	82.5	−810 ± 26	−248 ± 08
	TEGDPE	83.3	−704 ± 6	−249 ± 02
	TPEDA	84.3	−930 ± 35	−246 ± 09
	TPA	84.7	−960 ± 43	−250 ± 11
	TPEDEA	85.9	−825 ± 8	−238 ± 02
	TPTM	86.4	−740 ± 10	−237 ± 03

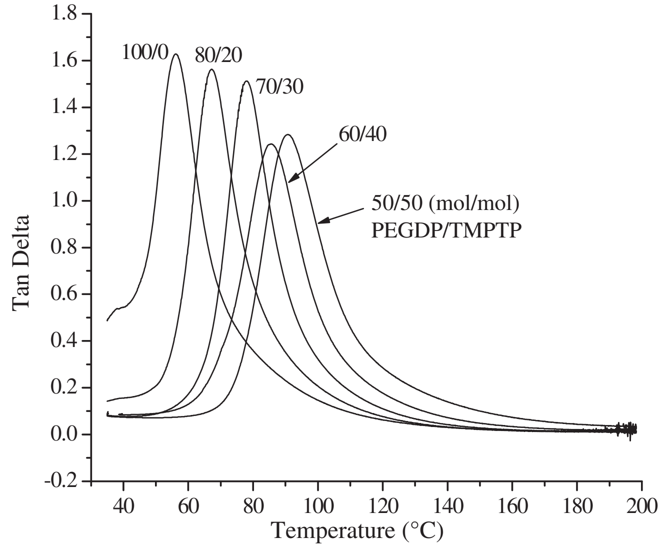

Fig. 10. Tan δ vs. temperature of DAHP-BPA cured using various mixtures of PEGDP and TMPTP. Samples were equilibrated and held for 5 min at 35 °C, and then heated at a rate of 2 °C/min to 200 °C.

composition. The data show that as the proportion of trifunctional alkyne is increased, the crosslink density and the resulting glass transition temperature increases. For the system containing 100% PEGDP the tan δ peak was found at 56 °C; while the system containing a 50/50 mixture of the two alkynes was found to have a tan δ peak at 90 °C.

4. Conclusion

With the goal of developing a low-temperature-cure composite resin system, we have developed a modified epoxy resin, derived directly from commercial DGEBA-type resins, e.g., EPON 825, that cures via triazole ring formation (Huisgen 1,3-dipolar cycloaddition reaction) rather than the traditional oxirane/amine reaction. Commercial DGEBA was easily converted to an azide-modified resin through reaction with NaN_3 in the presence of ammonium chloride. A series of di-, tri-, and tetra-functional alkynes, of various types, including propargyl esters, ethers, and amines, and propiolate esters, were synthesized to serve as chain extenders/crosslinkers for the resin; two of the synthesized alkynes, TPEDEA and TMBTP, were completely novel and not previously reported. Taking inspiration from azide/alkyne propellant binders, propargyl ester-based alkynes were initially synthesized. Their excessive reactivity led to the synthesis of slower acting propiolate esters. The latter compounds displayed more favorable reactivity profiles, but they still contained undesirable ester linkages and many were solid, leading to poor processability. The final two groups of alkynes, propargyl ethers and propargyl amines, circumvented all issues; they were found to possess relatively low reactivity, and they contain no labile linkages and are liquids. The propargyl amines showed the greatest promise for scale up and fabrication of both filled and unfilled composite samples because, in addition to the aforementioned advantages, they have high functionality and low equivalent weight. TPA was particularly attractive in this work, since it could be obtained commercially. Overall, the propiolate species were found to have E_a in the range of 70–74 kJ/mol; while the propargyl species were found to have E_a in the range of 82–87 kJ/mol. Though the propiolate species proved too reactive on their own, they could be combined with the less reactive propargyl species to achieve reactivity and properties tailored to specific applications.

Similarly, we demonstrated that by mixing varying amounts of difunctional ethylene glycol-based alkynes with tri- or tetra-functional species, crosslinking density and resulting physical and thermal properties of the systems can be manipulated. For example, by incorporating 20% PEGDP into a TMPTP/DAHP-BPA system, the tan δ peak was increased by 10 °C. Regardless of structure, all systems studied were very exothermic, between −200 kJ/mol and −265 kJ/mol, with the potential to allow for higher crosslink density prior to vitrification. Through the use of various combinations of these alkynes, a variety of systems were obtained with diverse reactivates, and thermal and physical properties.

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