Kinetics of Bulk Azide/Alkyne "Click" Polymerization

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ABSTRACT: A bulk step-growth polymerization of multifunctional azides and alkynes through the copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction is described. The polymerization kinetics of two systems containing different diynes, bisphenol E diyne (BE-diyne)/bisphenol A bisazide (BAbisazide) and tetraethylene glycol diyne (TeEG-diyne)/BA-bisazide, are evaluated by differential scanning calorimetry (DSC), shear rheology, and thermogravimetric analysis. The effects of catalyst concentration on reaction kinetics are investigated in detail, as are the thermal properties (glass transition and decomposition temperatures) of the formed polymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 4093–4102, 2010

KEYWORDS: alkyne; azide; "click" chemistry; differential scanning calorimetry (DSC); kinetics; rheology; self-healing

INTRODUCTION Since the copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) "click" reaction was introduced by Sharpless¹ and Meldal² independently in 2002, it has become a useful tool in the field of polymer and materials science for applications such as the synthesis of novel polymers and surface modification of nanoparticles or other substrates. Both alkyne (R—C=CH) and azide (R—N₃) groups are inert to most reactive moieties/functional groups, but in the presence of Cu (I) can combine to create triazole linkages³ (Fig. 1). The formed triazoles are chemically robust to such environmental conditions as oxidation, reduction, and hydrolysis.

Most reported applications of CuAAC "click" reactions in polymer synthesis are focused on connecting polymer fragments to form linear,^{4,5} star,^{6,7} dendrimer,^{8,9} and brush architectures.¹⁰⁻¹³ Step-growth polymerization by CuAAC "click" chemistry is reported less frequently. Linear conjugated polymers with regular triazoles backbones have been reported by Van Steenis et al.¹⁴ and Bakbak et al.¹⁵ through the polymerization of small diynes and bisazides. In addition to the diyne/bisazide strategies, a novel category of α -azide, ω -alkyne monomers was developed and applied to achieve "click" polymerization from a single monomer.¹⁶ While the "click" polymerizations described above were all conducted in solvents, Finn et al. directly applied multi-functional azide and alkyne monomers as adhesives between two copper plates, which yielded polymers with adhesive strengths higher than several commercial glues.^{17,18} To our knowledge, these adhesive studies are the only bulk (i.e., solvent free) "click" polymerizations that have been reported. Understanding the kinetics of the CuAAC reaction is important to gain insight into the reaction mechanism and to determine the

processing parameters for designing new materials. Rodionov et al. found that in solution, ligands, buffer salts, and substrates all significantly influence the kinetics of the CuAAC reaction in a complex manner.¹⁹ Additionally, Binauld et al. conducted kinetic studies of the step-growth click polymerization by ¹H NMR and showed that the click polymerization typically follows first order reaction kinetics.²⁰ While the CuAAC "click" based polymerization in solvent has been thoroughly investigated, the kinetics of the CuAAC "click" polymerizations in the bulk (solvent free) is an open area of research.

In our group, we are investigating CuAAC chemistry for selfhealing materials. The concept of self-healing materials, inspired by living biological systems, was first successfully demonstrated in 2001 by White et al.²¹ using Ru-initiated ROMP (ring-opening metathesis polymerization) to facilitate the healing response. Healing was achieved by embedding monomer-filled microcapsules into a polymer matrix. Upon damage-induced microcracking, the microcapsules rupture and release healing monomer into the crack plane where it is initiated by a chemical trigger, the Ru-based Grubbs' catalyst, which is also embedded in the matrix, to bond the crack faces closed. Encapsulated healing monomers have included norbornene-based monomers or their mixtures, which could be modified with appropriate cross-linking agents^{22,23} or carbon nanotube reinforcements.²⁴ In recent years, many additional approaches to achieve self-healing functionality in materials have been proposed. These strategies include "bleeding" microvascular systems,25 solid state systems requiring external energy to assist in the healing process,²⁶⁻²⁸ and force-induced activation of covalent bonds to repair damage.29

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FIGURE 1 Copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) "click" reaction.

While the Ru-initiated healing monomer systems in the first generation of self-healing materials worked well to demonstrate the concept, the cost of the material is very high due to its reliance on the expensive Ru-based Grubbs' catalyst. Typical self-healing composites contain \sim 2.5 wt % of first generation Grubbs' catalyst with 5 wt % healing monomerfilled microcapsules in an epoxy matrix, which adds significant cost to the self-healing material.³⁰ This cost is only expected to increase since the most expensive component, the Grubbs' catalyst, is based on a limited reserve of rare ruthenium.

A possible approach to overcome the cost barrier is to develop new healing monomer systems. "Click" chemistry has many of the features desired for self-healing chemistries: high-yielding reactions occurring at ambient or sub-ambient temperatures, harmless reagents, minimal and inoffensive byproducts formed, and no or benign solvents. All of these outstanding features meet the requirements of a successful healing monomer. More important, the overall cost of the self-healing materials based on "click" chemistry used herein is estimated to be about seven times less expensive than the Ru-based systems (based on current prices as of February 2010).

As mentioned above, the effect of such polymerization conditions as catalyst concentration, reaction temperature, and monomer composition on the kinetics of the bulk "click" polymerization have not been investigated. In this study, a difunctional bisazide (bisphenol A bisazide) and two different di-functional alkynes (bisphenol E diyne and tetraethylene glycol diyne) were synthesized. The CuAAC bulk polymerization was performed and monitored by differential scanning calorimetry (DSC). The effects of catalyst concentration on the cure kinetics were investigated in detail. Other important properties related to fabrication of selfhealing materials, such as the viscosity of the monomer mixtures (candidate healing monomers) and the thermal properties of the resulting polymers, are also investigated.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA) epoxy resin was purchased from Miller-Stephenson Chemical Co. (Danhury, CT) as EPONTM resin 828. All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used asreceived unless otherwise stated. The synthetic routes to the "click" monomers are shown in Figure 2.

Synthesis of Bisphenol A Bisazide (3,3'-(4,4'-(propane-2,

2-diyl)bis(4,1-phenylene))bis(oxy)bis(2-azidopropan-1-ol)) Epon 828 bisphenol-A epoxy resin (27.4 g, 0.07 mol) was dissolved in 300 mL methanol with rapid stirring. Ammonium chloride (11.26 g, 0.21 mol) and sodium azide (13.8 g, 0.21 mol) were dissolved in a separate 300 mL portions of methanol. These solutions were combined and refluxed for 12 h. The reaction flask was cooled, and the reaction mixture was concentrated to \sim 50 mL using a rotary evaporator and diluted with 250 mL deionized water. The product was extracted into diethyl ether (6 \times 100 mL) and the organic extracts were washed with brine (3 \times 50 mL). The solvent was evaporated to reveal 29.5 g (88.1%) of a viscous, yellow liquid. Azide product existed as two diastereomers, which were not further separated, and otherwise of good purity. ¹H NMR (400 MHz, CDCl₃) δ_{H} : 7.16 (m, 4H), 6.82 (m, 4H), 4.09 (m, 2H), 4.01 (m, 4H), 3.52 (m, 4H), 2.80 (br s, 2H), 1.65 (s, 6H) for the major diastereomer. ¹³C NMR (100 MHz, CDCl₃) δ_{C} : 156.2, 144.1, 128.1, 114.1, 69.2, 69.0, 53.6, 42.0, 31.3 for the major diastereomer and 156.2, 144.1, 128.1, 114.1, 109.3, 82.1, 66.1, 46.2, 15.5 from minor diastereomer. Mass spectrum: Found 426.72. C₂₁H₂₆N₆O₄ requires 426.47.

Synthesis of Bisphenol E diyne (4,4'-(ethane-1,1-diyl) bis((prop-2-ynyloxy)benzene))



4,4'-Ethylidenebisphenol (25 g, 0.117 mol) was dissolved in 500 mL dry acetone in a 2-neck, 1-L round bottom flask

FIGURE 2 Scheme of "click" monomer synthesis: BA-bisazide, BE-diyne, and TeEG-diyne.

	Sample	Catalyst Concentration ^a	𝒯 _g ^b (°C)	ΔH^{b}	
				(J/g)	(J/mol)
BE-diyne and BA-bisazide	B/B-1	1:640 (0.5 wt %)	78.6 ± 2.8	$554.4~\pm~5.5$	397.4 ± 3.9
	B/B-2	1:320 (1.0 wt %)	83.0 ± 2.8	552.9 ± 21.9	396.3 ± 15.7
	B/B-3	1:160 (2.0 wt %)	85.9 ± 1.8	584.5 ± 16.3	419.0 ± 11.7
TeEG-diyne and BA-bisazide	T/B-1	1:640 (0.5 wt %)	11.4 ± 2.9	577.5 ± 21.9	402.4 ± 15.3
	T/B-2	1:320 (1.0 wt %)	10.9 ± 1.7	532.2 ± 24.7	370.8 ± 17.4
	T/B-3	1:160 (2.0 wt %)	22.8 ± 1.5	565.6 ± 4.6	394.1 ± 3.2

TABLE 1 Summary of the Sample Compositions, T_q 's of "Click" Polymers, and Reaction Heats

^a Mole ratio of catalyst to monomer and approximate weight percent with respect to diyne in parentheses.

 $^{\rm b}$ Average values and standard deviations from the samples cured at different heating rates.

equipped with a magnetic stirring bar and reflux condenser. Propargyl bromide (30.55 g, 0.257 mol) was added in one portion, followed by addition of potassium carbonate (38.8 g, 0.280 mol). The mixture was stirred and refluxed for 24 h, at which point the reaction was complete. Solid impurities were removed by filtration and volatiles were evaporated under high vacuum to reveal 30.2 g (89.1%) of pure product as an orange, slightly viscous liquid. ¹H NMR (400 MHz, CDCl₃) δ_{H} : 7.18 (m, 4H), 6.94 (m, 4H), 4.68 (d, 4H), 4.11 (dd, 1H), 2.55 (t, 2H), 1.63 (d, 3H). ¹³C NMR (100 MHz, CDCl₃) δ_{C} : 156.0, 139.9, 128.7, 114.9, 79.0, 75.6, 56.0, 43.4, 22.4. Mass spectrum: Found 290.13. C₂₀H₁₈O₂ requires 290.36.

Synthesis of Tetraethylene Glycol Diyne

(4,7,10,13,16-pentaoxanonadeca-1,18-diyne)

Tetraethylene glycol diyne was synthesized by following a reported procedure³¹ with slight modifications. Hexane was dried by distillation over metal sodium and benzophenone. Sodium hydride (3.6 g of 60% in mineral oil, 0.090 mol) was decanted with dry hexane (50 mL) three times to remove mineral oil, and then dispersed in dry toluene (100 mL) with magnetic stirring. The suspension was transferred into a 2-neck flask and cooled to 0 °C in an ice bath. A solution of tetraethylene glycol (5 g, 0.026 mol) in toluene (20 mL) was added drop wise. The resulting mixture was stirred for 1 h at 0 °C until the deprotonation process was finished, followed by dropwise addition of propargyl bromide (11 mL, 0.123 mol). The reaction mixture was stirred at 0 °C for 6 h, and then warmed up to room temperature and quenched with saturated aqueous NH₄Cl (50 mL). The organic layer was separated and the aqueous layer was washed with CH_2Cl_2 (3 \times 50 mL). The organic extracts were combined, and the solvent was removed by rotary evaporator to reveal the crude product as a low viscosity, orange-brown color liquid. The product was purified by silica gel chromatography eluting with 1:1 ethyl acetate/methylene chloride to yield 3.1 g (45%) of a colorless liquid. ¹H NMR (400 MHz, CDCl₃) $\delta_{\textit{H}}\!\!:$ 4.20 (m, 4H), 3.68 (m, 16H), 2.42 (m, 2H). ^{13}C NMR (75 MHz, CDCl₃) δ_c: 79.8, 74.7, 70.8, 70.5, 70.3, 69.2, 58.6.

Sample Preparation and Characterization

Two alkyne/azide healing monomer systems were investigated. One is a mixture of bisphenol E diyne (BE-diyne) and bisphenol A bisazide (BA-bisazide); the other is tetraethylene glycol diyne (TeEG-diyne) and BA-bisazide. The alkynes and azides were mixed in a mole ratio of 1:1. To evaluate the effect of catalyst concentration, three samples of each alkyne/azide system were prepared with different catalyst molar concentrations of 1:640, 1:320, and 1:160. These mole ratios of catalyst to monomer are ~0.5, 1.0, and 2.0 wt % with respect to the mass of the diyne. The details of these sample compositions are listed in Table 1. The names of the samples are designated by their composition (B/B for the mixture of BE-diyne and BA-bisazide, T/B for TeEG-diyne and BA-bisazide) and catalyst concentration (1 for 0.5 wt % to 3 for 2.0 wt %). For example, TeEG-diyne and BA-bisazide with 1.0 wt % catalyst concentration is labeled as T/B-2.

To prepare the samples, the catalyst, bromotris(triphenylphosphine)copper(I) (Cu(PPh₃)₃Br), was weighed into a vial containing a magnetic stirring bar. Then, the desired amount of diyne (~0.3 g) was added. The vial was sealed and either warmed up to 45 °C in an oil bath (for BE-diyne) or processed at room temperature (for TeEG-diyne). After stirring for either 2 h (for the BE-diyne), or 10 min (for the TeEGdiyne), the catalyst was completely dissolved, and one equivalent of the BA-bisazide, relative to the diyne, was added to the mixture. The reaction mixture was then stored in a freezer at -13 °C for subsequent tests.

Reaction kinetics of bulk azide/alkyne "click" polymerization were evaluated by using a TA Instruments (New Castle, DE) Q20 differential scanning calorimeter (DSC) at various heating rates. A dry nitrogen flow of 50 mL/min was used as the purge gas for all DSC experiments. The liquid azide/alkyne and catalyst mixture (around 8 mg for each test) was transferred into TzeroTM hermetic aluminum pans using a pipette and sealed with a pin hole-pricked lid. For each composition, several samples were evaluated at multiple heating rates: 2, 5, 10, and 15 °C/min. Unless otherwise state, a second dynamic scan followed from -50 to 150 °C at a heating rate of 10 °C/min to evaluate the T_g of the formed polymer.

The rheological evaluation was conducted using a TA Instruments AR2000ex stress-controlled rheometer with parallelplate geometry and an aluminum plate fixture with a diameter of 25 mm and a 0.5 mm gap. A sample volume of 0.25 mL was



transferred to the bottom plate using a 1-mL syringe. Oscillatory experiments were used to monitor changes in viscosity with time at an isotherm of 120 °C. A 2-min equilibrium period was allowed for each sample to reach the test temperature before starting to collect data at an amplitude of 1000 Pa and 1 Hz for 2 h. Then, a temperature-ramp test was performed from 120 to 25 °C at a cooling rate of 1 °C/min.

The viscosity of the alkyne/azide mixtures (without catalyst) was tested on the same rheometer with a Peltier plate, utilizing a cone/plate geometry. The cone has a diameter of 40 mm, an angle of 1° and a truncation of 28 μ m. All of the tests were performed at 25 °C. The samples (0.3 mL) were transferred to the plates in the same manner mentioned earlier. A continuous flow test was conducted for each sample with the shear strain rate ramping linearly from 0.5 to 500 s⁻¹.

Thermogravimetric analysis (TG) was performed on a TG model Q50 (TA Instruments) to determine the decomposition temperature of the polymerized azide/alkyne healing monomers. Polymer samples, about 10 mg, were placed in a platinum pan and heated from 25 °C to 800 °C at a rate of 20 °C/min under an air flow at 60 mL/min.

RESULTS AND DISCUSSION

In the presence of the Cu (I) catalyst, the alkyne/azide mixture is expected to undergo a "click" step growth polymerization as shown in Figure 3. To analyze the progress of this "click" bulk polymerization, we performed reactions in a DSC cell and monitored the exothermic heat evolved in real-time.

Using a dynamic scan method, we are able to investigate the kinetics throughout the course of the reaction, and the kinetic parameters can easily be interpreted by a comparison of measurements at different heating rates.³² Figure 4 shows the typical dynamic scan data for the B/B-1 samples (BEdiyne/BA-bisazide, with 0.5 wt % catalyst) at heating rates of 2, 5, 10, and 15 °C/min. Integration of the peak (with respect to time) gives the reaction heat, ΔH , generated during reaction. The reaction heat shows a slight trend of higher ΔH with decreasing heating rate, but differences in each heating rate were very small with a nearly constant ΔH of 554.4 ± 5.5 J/g (397.4 \pm 3.9 J/mol). The reaction heats, averaged from different heating rate dynamic scans, for all samples are listed in Table 1. For the BE-diyne/BA-bisazide system, sample B/B-3 (highest catalyst concentration) has the highest reaction heat (ΔH), while the other two samples

FIGURE 3 Bulk polymerization of diyne and bisazide through CuAAC "click" reaction.

B/B-1 and B/B-2 have similar ΔH values. For the TeEGdiyne/BA-bisazide system, the situation is more complex. T/ B-1 has the lowest catalyst concentration but the highest reaction heat. However, given the standard deviations, all three T/B samples are considered to have similar reaction heats within experimental error.

Following each initial dynamic scan, a second dynamic scan at 10 °C/min was performed to evaluate the glass transition temperature (T_g) of the resulting polymer. The T_g is determined from the half-height position of the step-wise transition of the heat flow. As shown in Figure 5, the glass transition temperature appears to be a function of both the heating rate during the first dynamic scan and the catalyst concentration. Because the polymers from the BE-diyne/BAbisazide system contain the more rigid phenyl groups, their T_{g} 's are much higher than the polymers from TeEG-diyne/ BA-bisazide, which is dominated by the flexibility of the oligoethylene glycol units in the polymer chains. As mentioned before, the reaction heat measured at slower heating rates is slightly higher than those measured at faster rates. The higher reaction heat indicates that more alkyne and azide functional groups have undergone the CuAAC "click" reaction, which may result in a polymer with slightly higher molecular weights and a corresponding higher glass transition



FIGURE 4 DSC dynamic scan curves for B/B-1 system (BEdiyne/BA-bisazide, with 0.5 wt % catalyst) at heat rates of 2, 5, 10, and 15 °C/min (exothermal direction: up). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 The effects of heating rate during polymerization and catalyst concentration on the T_g of CuAAC formed polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature. By similar arguments, systems polymerized at higher catalyst concentrations react faster and result in polymer with higher T_{g} 's. As shown in Figure 5, the effect of catalyst is more pronounced for the TeEG-diyne/BA-bisazide system than for the BE-diyne/BA-bisazide system. The glass transition temperature for each composition is listed in Table 1 as the average of the values obtained from the samples polymerized at different heating rates.

It can be seen from Figure 4 that the peak temperature, $T_{\rm p}$, is shifted to higher temperatures with increasing heating rate, β . Assuming the maximum reaction rate, $d\alpha/dt$, occurs at $T_{\rm p}$, where $d\alpha^2/dt^2$ equals zero, the kinetic equation can be expressed as:

$$\ln\left(\frac{\beta}{T_{\rm p}^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_{\rm p}} \tag{1}$$

where *R* is the universal gas constant in 8.314 J K⁻¹ mol⁻¹. This expression is known as Kissinger's equation,³³ where a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ gives the values of the pre-exponential factor *A* and activation energy *E* from the intercept and the slope of the linear fit, respectively. Figure 6 shows such a plot for the B/B-1 sample by using the values of T_p marked in Figure 4. The linear fit has a coefficient of determination (R^2) greater than 0.99 and gives an activation energy as 73.4 kJ/mol.

To compare the complex effect of catalyst concentration on the bulk "click" polymerization, the DSC curves of the samples with different catalyst concentrations are plotted together in Figure 7. All of the curves plotted in the figure were obtained at the same heating rate (10 °C/min). For the BE-diyne/BA-bisazide system, the dynamic scan curves show a shoulder at the low temperature side of the major exothermal peak as indicated by arrows. The shoulder becomes



-13.5

FIGURE 6 Kissinger's plot for B/B-1 system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more pronounced with increasing catalyst concentration and becomes the dominant peak at the highest catalyst loading. It is well known that bisazides and diynes can undergo a thermal step growth polymerization without catalyst at elevated temperatures.^{34–36} Therefore, a BE-diyne/BA-bisazide sample was tested in the absence of catalyst at the same conditions, and the resulting DSC dynamic scan is shown as a thin solid line in Figure 7. The peaks at around 140 °C in the copper-catalyzed systems occur at the same temperature as the singular peak in the uncatalyzed system and are therefore attributed to thermal polymerization, while the lower temperature shoulders are facilitated by the copper catalyzed reaction. For the TeEG-diyne/BA-bisazide system, the effect of catalyst concentration does not follow the same



FIGURE 7 Effect of catalyst concentration on the "click" polymerization at a heating rate of 10 °C/min (exothermal direction: up). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 8 Multiple-peak fits of the dynamic scanning curves for B/B-2 system at heating rates of 2 and 15 °C/min (offset to back). Symbols: experimental data. Solid and dash lines: fitting results. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

trend as in the BE-diyne/BA-bisazide system. The major exothermal peak remains almost constant, regardless of catalyst concentration (not shown here).

The dynamic scan curves of B/B-2 and B/B-3 samples are likely a sum of two separate peaks. To further investigate the effect of catalyst concentration, the experimental DSC curves are fitted as the sum of two Gaussian peaks. Examples of these fitting results are shown in Figure 8, in which the DSC scans of B/B-2 at the slowest and fastest heating rates are presented. At 2 °C/min two peaks of similar heights are observed, whereas the 15 °C/min curve has a second peak much larger than the first. By analyzing the peak temperatures from the first peak (Peak 1) and the second peak (Peak 2) separately in Kissinger's equation, two distinct activation energies are obtained as shown in Figure 9 and listed in Table 2. For the B/B-2 system, the two activation energies for each peak have a similar value about 63 kJ/mol, and they are slightly higher than the overall value of 58.6 kJ/mol, which is calculated from the peak temperatures of the original dynamic scan curves. On the whole, the *E* decreases with increasing catalyst concentration for the B/B-1 and B/B-2 samples, and then increases for the B/B-3 sample. This abnormal trend indicates a change of reaction kinetics with conversion, which we will discuss later. For the T/B system, the activation energy of TeEG-divne/BA-bisazide decreases with increasing catalyst concentration, similar to what was observed for the BEdiyne/BA-bisazide system.

The conversion α can be experimentally measured by DSC, where the conversion at any given time (*t*) is defined as the enthalpy of reaction up to time *t* divided by the total enthalpy of reaction.³⁷ If activation energy is not assumed to be constant throughout the reaction, but instead is a function of conversion, the isoconversional analysis developed by



FIGURE 9 Kissinger's plot of B/B-2 and B/B-3 samples. The peak temperatures are estimated from the multiple-peak fittings of the original dynamic scan data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ozawa can be applied to give a simple relationship between the conversion dependent activation energy, E_{α} , heating rate, and temperature:³⁸⁻⁴¹

$$\log \beta = -\frac{0.4567E_{\alpha}}{RT_i} + A' \tag{2}$$

where T_i is the temperature required to reach a given monomer conversion (*i*). For each degree of conversion, A' is a constant that can be expressed as

$$A' = \log\left[\frac{AE_{\alpha}}{g(\alpha)R}\right] - 2.315 \tag{3}$$

and $g(\alpha)$ is a conversion dependent function. Similar to Kissinger's linear regression approach, a plot of log β versus 1/ T_i at each conversion gives a slope proportional to the corresponding activation energy at that conversion (Fig. 10). Furthermore, the relationship between activation energy and conversion can be obtained (Fig. 11) to provide additional

 TABLE 2
 Summary of the Activation Energies and Other

 Kinetic Parameters
 Parameters

Sample	<i>E</i> (kJ/mol)	In <i>A</i> ª	nª	mª	n + m
B/B-1	73.4	16.6	1.2	0.0	1.2
B/B-2	58.6 (63.8, 62.4) ^b	12.4	1.2	0.0	1.2
B/B-3	63.0 (74.5, 58.4) ^b	15.2	1.8	0.1	1.9
T/B-1	79.4	18.1	1.3	0.0	1.3
T/B-2	76.8	17.3	1.2	0.0	1.2
T/B-3	71.7	15.8	1.3	0.0	1.3

^a Average values from the fitting parameters of original experimental data.

^b The values in parentheses represent the activation energies calculated from the multiple-peak fittings.



FIGURE 10 Ozawa's plot for B/B-1.

information about the change in reaction kinetics throughout the polymerization. On the whole, the activation energy of the BE-diyne/BA-bisazide system is lower than the TeEGdiyne/BA-bisazide system, suggesting that the BE-diyne/BAbisazide is more reactive towards "click" polymerization. In agreement with the results from Kissinger's approach, the increase of catalyst concentration decreases the activation energy. For the TeEG-diyne/BA-bisazide system, the E_{α} remains constant throughout the polymerization. For the BEdivne/BA-bisazide system, this relationship is more complicated. B/B-1 and B/B-2 samples follow a similar trend-an increase in E_{α} is observed with increasing conversion—suggesting that at least two parallel reactions are involved.⁴² The E_{α} for the B/B-3 sample, however, initially decreases with monomer conversion, and after reaching a minimum value at 60% conversion, it slightly increases. This decreasing concave shape of the E_{α} versus conversion curve suggests that higher catalyst concentrations may induce competing reaction pathways, relative to lower catalyst loadings.⁴¹



FIGURE 11 E_a versus conversion for both BE-diyne/BA-bisazide and TeEG-diyne/BA-bisazide systems.

Generally, the rate of conversion is a function of the concentration of unreacted materials and can be expressed by one of two common models: *n*th order and autocatalytic, respectively:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \tag{4}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \alpha^m \tag{5}$$

where α is conversion, *n* and *m* are reaction orders, and *k* is the temperature-dependent reaction rate constant given by Arrhenius relationship:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \tag{6}$$

The *n*th order model, eq. 4, indicates that the maximum conversion rate occurs at the beginning of the reaction ($\alpha = 0$), while the autocatalytic model, represented by eq. 5, reaches a maximum value at an intermediate conversion. If the reaction order *m* equals to zero, the autocatalytic model collapses into the *n*th order model.

The heat flow dH/dt measured by DSC is related to the conversion rate by the following equation.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}H/\mathrm{d}t}{\Delta H} \tag{7}$$

By combining eqs. 5–7, the heat flow can be expressed as

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \Delta HA \exp\left(-\frac{E_{\alpha}}{RT}\right) (1-\alpha)^n \alpha^m \tag{8}$$

where ΔH is the reaction heat, obtained from the integration of the dynamic scan curves. As mentioned before, the



FIGURE 12 Dynamic scanning curves and autocatalytic model fits of T/B-3 system at different heating rates, where the heat flow is normalized with respect to heating rate. Symbols: experimental data. Lines: autocatalytic model fits (exothermal direction: up).



FIGURE 13 Shear loss modulus G'' versus temperature for poly (B/B) and poly (T/B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

activation energy remains almost constant for the TeEGdiyne/BA-bisazide system and slightly varies with conversion for the BE-diyne/BA-bisazide system. Therefore, using the constant activation energy calculated from Kissinger's approach is a good approximation. By applying the values of ΔH and *E* listed in Table 1 and Table 2, eq. 8 can be used to fit the experimental data of the DSC dynamic scans, shown in Figure 12 for the T/B-3 sample, where the dynamic scan curves are normalized with respect to heating rate. The model curves fit the experimental data reasonably well throughout most of the temperature range with $R^2 > 0.95$, but deviates in the beginning of the reaction, where the small shoulder is not captured by the model.



FIGURE 14 TG results of the "click" polymers, poly (B/B) and poly (T/B), at a heating rate of 20 °C/min in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These models provide the pre-exponential factor A, and the reaction orders n and m, which are listed in Table 2. For all samples except B/B-3, the reaction order m is close to zero, indicating that the bulk click polymerization follows nth order reaction kinetics. As mentioned in the discussion of the relationship between activation energy and conversion, the B/B-3 system displays a different trend from the other two BE-diyne/BA-bisazide systems. Correspondingly, the B/B-3 follows autocatalytic reaction kinetics, which has a different reaction order of n = 1.8, compared to 1.2 for the other samples, and a non-zero reaction order m.

The resulting polymers show poor solubility in THF. The poly (B/B) can be partially dissolved; while, the poly (T/B) only swelled and gave no sign of dissolving after immersion in THF at room temperature for one week. In CDCl₃, both poly (B/B) and poly (T/B) can only be partially dissolved, resulting in cloudy solutions. The polymers can be dissolved in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) completely. ¹H NMR spectra of the click polymers in *d*-DMSO show the appearance of the triazole-ring proton peak at 7.7 ppm, which confirms the polymerization of the monomers. The peak of the alkyne protons at 2.5 ppm does not completely disappear, indicating that dissolved parts of the polymers contain low moleculer weight polymer or oligomer, in which the end groups of the alkyne proton are more pronounced.

The resulting polymers were further characterized by torsional dynamic mechanical analysis (DMA) in a controlled stress rheometer. As expected, at an isotherm of 120 °C, both the B/B and T/B systems exhibit an increasing viscosity with cure time. After these systems were fully cured for 2 h at 120 °C, the temperature was ramped down from 120 to 25 °C at a cooling rate of 1 °C/min while the shear storage modulus, *G'*, the shear loss modulus, *G''*, were recorded. The shear storage moduli at room temperature are measured as 1.1 and 0.9 MPa, for poly (B/B) and poly (T/B), respectively.



FIGURE 15 Comparison of viscosities of "click" monomers at a shear rate of 100 s⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 13 gives the plot of shear loss modulus versus temperature, the peak value of which is generally a good indication of the glass transition temperature. The $T_{\rm g}$ obtained from the peaks are 97.1 and 41.7 °C, for poly (B/B) and poly (T/B), respectively. After these torsional dynamic mechanical analysis experiments, DSC samples were prepared from the resulting polymers and evaluated in dynamic scan DSC experiments at 10 °C/min. There is no exothermic peak present in the resulting DSC curve, which indicates that the bulk polymerization was complete. The glass transition temperatures measured by DSC are about 20 °C lower than the values measured by DMA.

The thermal stability of the resulting "click" polymers was evaluated by using thermogravimetry (TG). The samples were heated to 800 °C at 20 °C/min with an air purge (Fig. 14). The temperature at the 5% mass loss is taken as the decomposition temperature, T_d . It was found that T_d is not significantly affected by such polymerization conditions as heating rate or catalyst concentration. The T_d of poly(TeEG-diyne/BA-bisazide) is 320 °C and slightly higher than that of poly(BE-diyne/BA-bisazide), 318 °C. Since the poly (T/B) contains the less stable tetraethylene glycol groups in the backbone of the polymer chains, they are less stable and decompose faster than the poly (B/B) as shown as a steeper drop on the TG curve in the temperature range between 300 and 450 °C. Above 700 °C, both polymers are completely degraded, with no residual char.

For self-healing materials, the viscosity of the healing monomer must be low to achieve successful self-healing. A low viscosity healing monomer can flow freely into a damage region and easily diffuse to the tips of the growing microcracks. Viscosity tests were performed on a rheometer with a cone/plate geometry. Five samples were tested: the three monomers and the two mixtures of alkyne and azide (1:1 mole ratio). A continuous flow test was conducted for each sample with shear rate ramping linearly from 0.5 to 500 s⁻¹. For all samples, the viscosity measured is independent of the shear rate and remains constant throughout the test, which is expected for a Newtonian fluid. Consequently, only the viscosity at a shear rate of 100 s^{-1} is presented in the Figure 15. The BA-bisazide viscosity is c.a. 59 Pas at 25 °C, and much higher than the two diynes. The diynes exhibit viscosities of 0.2 and 0.01 Pas for the BE-diyne and TeEG-diyne, respectively. As a result, the mixture of TeEG-divne/BA-bisazide has a much lower viscosity than the mixture of the BEdiyne/BA-bisazide. The lower viscosity of the former likely explains its superior catalyst dissolution: the catalyst Cu(PPh₃)₃Br can be easily dissolved in the mixture of TeEGdiyne/BA-bisazide at room temperature in less than two minutes.

CONCLUSIONS

With the goal of developing monomer systems for low-cost self-healing applications, one azide and two alkynes were synthesized. These materials were polymerized through a bulk copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction. The polymerization kinetics for these two systems,

and the effect of catalyst concentration, were investigated with DSC dynamic scans. For both the BE-diyne/BA-bisazide and TeEG-diyne/BA-bisazide system, the polymer $T_{\rm g}$ increases with increasing catalyst concentration and decreasing heating rates. Since oligoethylene glycol groups are more flexible than rigid phenyl groups, the $T_{\rm g}$ of poly (T/B) is much lower than poly (B/B). The effect of catalyst concentration on the reaction kinetics is complicated. Overall, the activation energy decreases with increasing catalyst concentration for both systems. The kinetic model developed suggests that the bulk "click" polymerization follows nth order reaction kinetics with a reaction order of about 1.2 for all samples except B/B-3, which follows autocatalytic reaction kinetics and has a total reaction order (n + m) of 1.9. The resulting polymers were confirmed by ¹H NMR and evaluated by rheological experiments. In the thermogravimetry analysis, the catalyst concentration and heating rate do not show significant effects on the thermal stability of the resulting polymers. Both systems have a decomposition temperature of about 320 °C in air. Furthermore, the TeEG-diyne has a very low viscosity, making the TeEG-diyne/BA-bisazide system attractive for self-healing applications.

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