Synthesis and Curing of Hyperbranched Poly(triazole)s with Click Polymerization for Improved Adhesion Strength

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ABSTRACT We successfully synthesized hyperbranched poly(triazole)s by in situ click polymerization of diazides **1** and triyne **2** monomers on different metal surfaces (copper, iron, and aluminum) and characterized their adhesive properties. Optimizations were performed to obtain high adhesive strength at different temperatures by analyzing the effects of curing kinetics, annealing temperature and time, catalyst, monomer ratio, surface conditions, alkyl chain length of diazides **1**, etc. The adhesive bonding strength with metal substrate is 2 orders of magnitude higher than similar hyperbranched poly(triazole)s made by click polymerization and clearly higher than some commercial adhesives at elevated temperatures. With the same conditions, adhesives prepared on aluminum and iron substrates have higher adhesive strength than those prepared on copper substrate, and an excess of triyne **2** monomer in synthesis has greater adhesive strength than an excess of diazide **1** monomer. Tof-SIMS experiment was employed to understand these phenomena, and the existence of an interphase between the polymer and metal surface was found to be critical for adhesive bonding with thicker interphase (excess of triyne **2** monomer) and the higher binding energy between polymer atoms and substrate atoms (e.g., aluminum substrate) generating the higher bonding strength. In addition, the light-emitting property of synthesized polymers under UV irradiation can be used to check the failure mode of adhesive bonding.

KEYWORDS: click polymerization • hyperbranched poly(triazole)s • light emission • adhesion strength • high-temperature adhesive

INTRODUCTION

Synthesis of 1,2,3-triazoles by 1,3-dipolar cycloaddition of azides and alkynes was discovered by Arthur Michael at the end of the 19th century (1) and significantly developed by Rolf Huisgen in the 1960s (2–5). This area of research was quiescent until the "click" reactions and the copper-catalyzed Huisgen reactions between azides/alkynes were discovered and formulated (6–9). The reactions have many advantages, which include (I) being sufficiently high yielding, (II) having high tolerance to functional groups, (III) being insensitive to reaction media, regardless of their protic/aptrotic or polar/nonpolar character, and (IV) being able to react at various types of interface, i.e., solid/liquid, liquid/liquid, and solid/solid interfaces (10–18).

Synthesizing hyperbranched polymers by the self-condensation of AB_n monomers has some limitations, because AB_n monomers are usually obtained via tedious synthesis approaches necessary for asymmetric functionality (19–21). Moreover, AB_n monomers are difficult to prepare and purify and suffer from self-oligomerization during storage under ambient conditions (20, 21). The $A_2 + B_3$ type of polymerization has been demonstrated to be an alternative route for hyperbranched polymers, as the monomers are easily obtained and free of the self-oligomerization problem encountered in the AB_n system. Still, the preparation of hyperbranched polymers requires multistep reactions and tedious product isolation, and long reaction times and poor product solubility are major obstacles (22, 23).

In our previous work (24), we developed hyperbranched poly(triazole)s by click polymerization by an $A_2 + B_3$ approach using easy-to-make and stable-to-keep diazide (A_2) and triyne (B_3) as monomers. The A_2/B_3 monomers were readily polymerized by metal-mediated click reaction and thermally catalyzed Huigen cycloaddition. It is important to know that in the absence of a transition-metal catalyst, their reactions are not regioselective and when catalyzed with Cu and Ru transition-metal salts, click polymerization produces hyperbranched polymers with regular 1,4- and 1,5-linkages, respectively, as shown in Scheme 1. Both polymers are soluble in common solvents such as dichloromethane (DCM), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO), repre-

Scheme 1. Syntheses of Hyperbranched Poly(triazole)s by Click Polymerizations of Diazides (A2) and Triynes (B3)

A2

1(m) (m = 4, 6)

B3
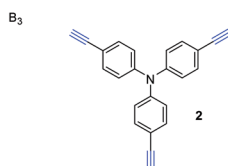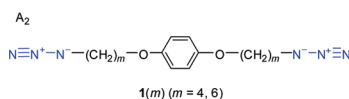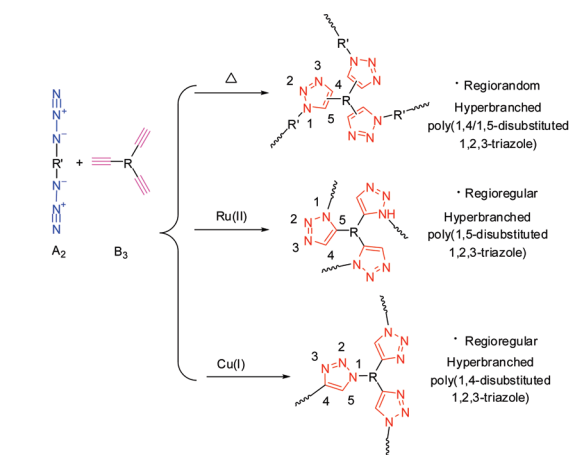
Polymer	1(m)	2
hb-**P1(4)/2**	1	1
hb-**P1(6)/2**	1	1
hb-**P1(6)/2-1**	4	3
hb-**P1(6)/2-2**	2	3

senting the first examples of hyperbranched poly(triazole)s with region-regular structures and macroscopic processability.

Joining metal members by adhesive bonding has numerous advantages over other techniques such as welding, soldering, and mechanical fastening, which include reducing weight, improving fatigue resistance, providing uniform stress distribution and potentially reducing cost (25). Triazoles have long been known for their strong affinity for metal ions and surfaces, which makes them popular components of polymers used as metal coatings and adhesions. The metal adhesive qualities of polymeric 1,2,3-triazoles have been demonstrated by many researchers (26–28). Polymer structures containing triazoles have been found to enhance binding to copper. Sharpless and co-workers (29, 30) found that Cu (I) species could efficiently catalyze the azide/alkyne "click" reaction and create a strong affinity with copper surfaces. The increase in reaction rate is mostly explained by the promotion of the formation of the Cu(I)—acetylide, reduction in the oxidation of the Cu(I) species, and prevention of side reactions of the acetylenes (31–33).

In this study, we prepared hyperbranched poly(triazole) adhesives from diazides and trialkyne deposited directly on metal surfaces catalyzed by transition metals and a purely thermal ("Huisgen-type") process. Various aspects to increase the strength of adhesive bonding at the interface between the polymers and the metal substrates were analyzed. Tof-SIMS was employed to understand the underlying behaviors.

EXPERIMENTAL SECTION

Sample Preparations. Unless otherwise stated, all the chemicals used in this study were purchased from Aldrich. The 1,4-
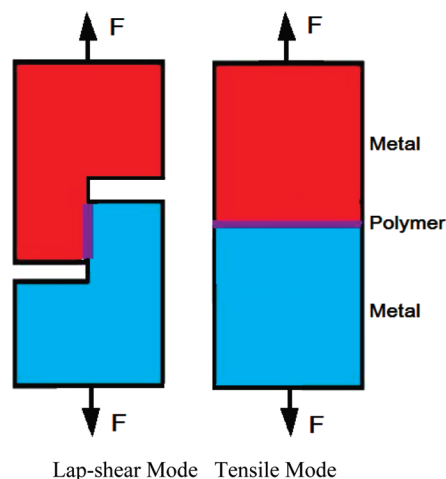

FIGURE 1. Schematic set-ups for the lap-shear and tensile experiments.

bis(4-azidobutoxy)benzene (A$_2$, $m = 4$), 1,4-bis(6-azidohexyloxy)benzene (A$_2$, $m = 6$), and tris(4-ethynylphenyl)amine (B$_3$) were prepared using published procedures and purified by silica gel columns (24, 34). The A$_2$ and B$_3$ monomers prepared in the present work are stable and can be stored in a dark place at room temperature for a long period. No structural changes caused by such undesired reactions as self-oligomerization were observed after the monomers had been kept in our laboratories for more than 6 months. Fresh stock solutions of the monomers in THF were prepared just before use; 0.9 M concentration of azide groups was used. The molar concentration of alkyne groups was used according to the functional group molar ratio listed in Scheme 1.

Gray cast iron (HT 200, China), yellow brass (H62, China), and aluminum alloy (6163, China) were used as substrates. Surfaces of iron, copper, and aluminum were abraded briefly using SiC sheet (240 grit) sandpaper until uniformly shiny, to remove surface contaminants and exhibit similar surface roughness (nominal surface roughness of $R_a = 52\ \mu m$, ISO 1302), followed by thorough rinsing with water and acetone, and then allowed to dry in ambient air and stored in a dry container.

Characterizations. In a typical procedure for adhesive bonding, approximately 0.55 mL of azide and alkyne solutions for a lap-shear test (0.41 mL for a tensile test) were deposited immediately onto one of adherend, when the other one was used to mix the solutions. For the tensile test, one adherend was laid vertically on the other and the thickness of adhesive layer was approximate $300-400\ \mu m$, whereas for the lap-shear test, two adherends were clamped together and the thickness of adhesive layer was approximate $100-135\ \mu m$. The surface bonding area was approximately 1242 mm^2 for lap-shear test, whereas it was 315 mm^2 for tensile test, as shown in Figure 1. The failure test was performed on a standard Instron 5500 universal testing machine. The cross-head rate was 2.54 mm/min for all the experiments. The results were found to be quite reproducible, with the standard deviation obtained from at least three independent measurements. No precautions were taken to exclude oxygen. No catalyst was added in the click reaction for purely thermal processes. An amount of approximately 1.37 mol % transition-metal salts: Cu (PPh$_3$)$_3$Br and Cp*Ru(PPh$_3$)$_2$Cl, respectively, were used for the catalyst-polymerization process, shown in Scheme 1.

Thermal stability was evaluated by measuring thermogravimetric analysis (TGA) thermograms on a Perkin-Elmer TGA 7 under air atmosphere at a heating rate of 20 °C/min.

The thin film specimens used in Time-of-flight-Secondary Ion Mass Spectrometry (Tof-SIMS) experiment were prepared as follows: The thin film metal substrates (aluminum and copper

foils) were rinsed by deionized water and acetone, followed by drying in a vacuum at 100 °C for 12 h. The monomer solutions with the particular ratios were spin-coated onto the treated surfaces of the thin films at a spin-coating speed of 4000 rpm. Specimens were cured in the optimized condition (125 °C for 8 h; this condition will be discussed in the later section) before characterization. Tof-SIMS is an important method for gaining better understanding of adhesives interface or interphase, especially when there is chemical reaction between adhesive and substrate. The Tof-SIMS depth profile measurements were obtained from a Phyical Electronics PHI 7200 Tof-SIMS spectrometer. The primary Cs^+ ion source was operated at 3 KV. Spectra acquisition was performed over a 150 × 150 μm^2 sample area. Charge compensation was realized by low-energy (0−70 eV) electron flooding.

Previous studies also show that these kinds of hyperbranched poly(triazole)s are light-emitting materials, because of their high luminescence and hole-transporting efficiency (24, 35). Fluorescent images were readily generated by UV irradiation of the polymer films after mechanical test and were used to check the coverage of the in situ polymerization polymers on the metal surfaces and the failure mode of adhesives during test.

RESULTS AND DISCUSSION

The successful formation of an adhesive on a metal surface requires two procedures: formation of a polymer and binding of the polymer with the metal surface.

Formation of a Polymer. In the formation of polymers, the reaction is a fusion process leaving no byproducts. This chemistry may therefore be expected to provide efficient polymer formation and the possibility of highly active catalytic domains in the developing polymer to enhance cross-linking, which will also favor binding with the metal surface. Cross-linked polymer was conveniently synthesized from the A_2 and B_3 components 1 and 2, as shown in Scheme 1. The [3 + 2] cycloaddition of these units provides 1,2,3-triazoles, which are noteworthy for their pseudoaromatic nature (providing the ability to engage in π-stacking), large dipole moment, and excellent hydrogen-bonding ability, so they are extraordinarily stable to other chemical reagents, high temperatures, oxidation, and reduction.

The formation of a polymer, as described in our previous study, can be accomplished by thermal polymerization and catalyst-polymerization (24, 35). We found that triyne 2 could undergo thermal polymerization with diazides 1 in a polar solvent to produce high-molecular-weight polymers with region-random structure, as shown in Scheme 1, and macroscopic processability with good yields, albeit at a slow rate. For example, reaction in a dioxane for a long period (e.g., 72 h) at 101 °C resulted in the formation of polymeric products with an M_w value of 177 500 (by the LLS technique) and 75.7 % yield (diazides 1 with $m = 6$). In the presence of the copper(I) catalyst held under the conditions of 60 °C in dimethylformamide (DMF) for 1.33 h, 1,4-disubstituted 1,2,3-triazoles were isolated in ∼ 51.6 % yield with measured M_w value of 5000, indicating moderate reactivity. The click reactions catalyzed by Cp*Ru(PPh$_3$)$_2$Cl produced 1,5-disubstituted 1,2,3-triazoles with higher yielding (∼75.0 %) and the measured M_w value of 9400 at 60 °C in THF for 0.5 h.

Binding of the Polymer with the Metal Substrate. Both tensile and lap-shear tests (will be discussed
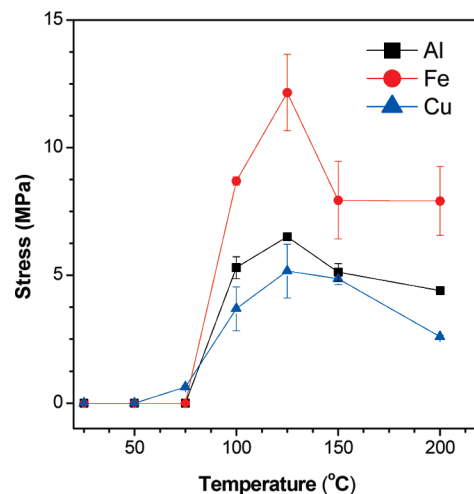

FIGURE 2. Curing temperature effect on lap-shear strength of *hb*-P1(6)/2 prepared by in situ thermal polymerization on different metal surfaces for 8 h.

in the later sections) conclude that the combination failure mode (adhesive failure and interface failure) is the failure mode of the adhesive bonding between our system and different substrates (see Figure 11 in detail). For binding a polymer of in situ click polymerization with a metal surface, besides mechanical locking, two factors are important: the number of arms of the monomeric unit and the presence of an amine group. Here, we fixed our monomeric unit and optimized the process to obtain the maximum adhesive strength in this kind of hyperbranched poly(triazole)s with the influence of curing kinetics, catalysts, annealing temperatures and time, substrates, molar ratios of monomeric unit, and test modes.

Effect of Curing Kinetics. Figure 2 shows the effect of curing temperature on lap-shear strength of *hb*-P**1**(6)/**2** prepared by in situ thermal polymerization on different metal surfaces for 8 h. As evident from the graph, when the curing temperature is low (<75 °C), none of the bonds have adhesive properties, which means that hyperbranched poly(triazole)s have not yet formed (or only a small amount has formed) after 8 h. When the temperature increases to 75 °C, only the copper bond has lap-shear strength, with the value of 0.62 ± 0.06 MPa, and the iron and aluminum bonds have none. This occurs because the Cu(II) created by oxidation of the surface metal with the pure Cu(0) surface forms active Cu(I) at the metal surface, which acts as a catalyst to accelerate the reaction in standard click reaction conditions (the rate of acceleration is about 1 × 10^5). A sufficient amount of hyperbranched polymer was formed by the self-generated catalyst and bound with the copper surface to obtain adhesive strength. Without the presence of a transition-metal catalyst, little adhesive polymer generates on the iron and aluminum substrates and no adhesive property is obtained. When the curing temperature is increased, all the bonds show adhesive properties, with iron displaying the highest lap-shear strength, followed by aluminum and copper. In the absence of a transition-metal catalyst, the reaction requires a high temperature to reach acceptable yields and to bind with metal surfaces to develop an adhesive bonding.
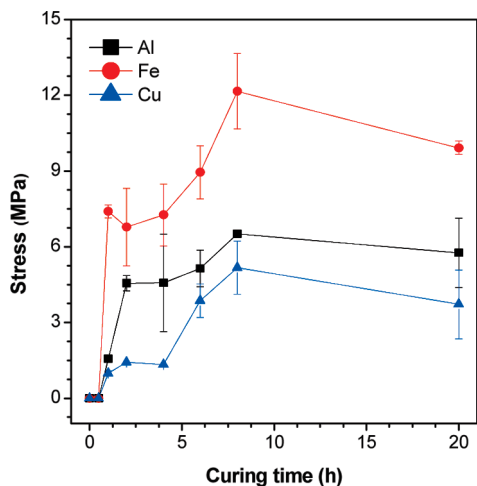
FIGURE 3. Curing time effect on lap-shear strength of *hb*-P**1**(6)/**2** prepared by in situ thermal polymerization on different metal surfaces at 125 °C.

FIGURE 4. Catalyst effect on lap-shear strength of *hb*-P**1**(6)/**2** prepared by in situ polymerization on different metal surfaces at different temperatures for 8 h. Cu catalyst: Cu (PPh₃)₃Br, 1.37 mol % in whole monomer solutions. Ru catalyst: Cp*Ru(PPh₃)₂Cl, 1.37 mol % in whole monomer solutions.

From Figure 2, 125 °C is the optimal curing temperature for hyperbranched poly(triazole)s on all the substrate surfaces. In the following experiments, therefore, we use this temperature for curing.

Figure 3 shows the effect of curing time on lap-shear strength of *hb*-P**1**(6)/**2** prepared by in situ thermal polymerization on different metal surfaces at 125 °C. As mentioned before, high temperature and sufficient time are needed for thermal curing. From the curves, within 1 h, adhesive strength is already sufficiently high, especially on the iron surface, where it reaches 7.4 ± 0.25 MPa. With the increase in time, the adhesive strength reaches a plateau, and then at 8 h increases to the highest values of 12.16 ± 1.5 MPa for iron, 6.51 ± 0.04 MPa for aluminum, and 5.17 ± 1.05 MPa for copper. Finally, the adhesive strength plateau with a little decrease in value is obtained, which may be caused by high-temperature oxidation for a long period of exposure in air without protection.

Effect of Catalysts. Figure 4 shows the effect of a catalyst on lap-shear strength of *hb*-P**1**(6)/**2** prepared by in situ polymerization on different metal surfaces at different temperatures for 8 h. Approximately 1.37 mol % transition-metal catalyst was added along with monomer solvents on the different metal surfaces. With similar results, at low elevated temperature (75 °C or lower), pure thermal curing does not generate adhesive strength on the metal surfaces. But with the addition of the transition-metal catalysts, the in situ polymers develop sufficient adhesive properties on the metal surfaces. In situ formed adhesive catalyzed by Ru(II) shows the highest lap-shear strength. [Cp*RuCl] compounds emerge as the most efficient and regioselective catalysts, as reported elsewhere (36, 37). When the curing temperature reaches 125 °C, poly(triazole)s synthesized by pure thermal polymerization come to the fore and display the highest strength. Similar to the results obtained at 75 °C, the adhesives generated by the Ru(II)-catalyst reaction have even better lap-shear strength than the Cu(I)-catalyst polymers on the same metal surface,
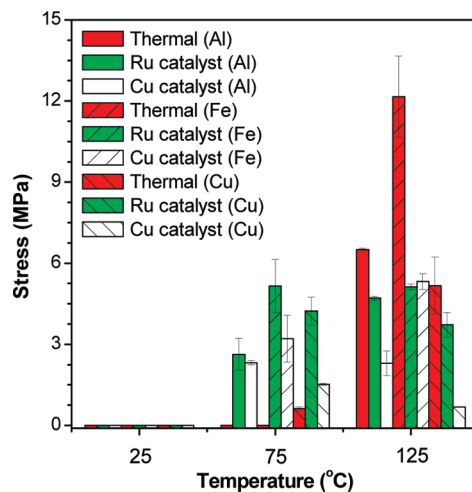
revealing a greater substrate tolerance of the Ru(II) catalyst than the Cu(I) catalyst.

Metallic catalysts have been widely used in polymerization reactions, but their complete removal from the resultant polymer has been very difficult. We tried to remove the catalyst residue by washing the hyperbranched polymers with amine solvents, but the results were unsatisfactory because of the poor solubility of the polymers in the hydrophilic solvents. Moreover, the preparation of the Ru(II) complex is a nontrivial task that requires high synthesizing skills. The most important finding was that the adhesive polymers synthesized by metallic-catalyzed reactions exhibited no improved adhesive strength than those created by purely thermal processes. In the following experiments, therefore, only in situ thermal polymerization on the metal surfaces was performed and optimized.

From the above experiments, we obtained 125 °C and 8 h as the optimal curing condition for lap-shear and tensile strengths. We then compared the adhesive properties of our system with available commercial products and with materials reported by other researchers using the click reaction for adhesive applications.

Figure 5 shows comparisons of tensile strength of *hb*-P**1**(6)/**2**-1 with commercial adhesives and materials from reference papers on a copper surface. The experimental data relating to commercial adhesives were drawn from reference papers (29, 30). As evidenced from the graphs, our system has the highest adhesive strength (16.49 ± 1.21 MPa). Its adhesive strength is much superior to that of the commercial products, being 127 times higher than Weld-It, 55 times higher than Amazing Goop, and 6 times higher than J-B Weld. The highest adhesive strength found for the click polymerized $A_2 + B_3$ approach using 2,2-bis(azidomethyl)propane-1,3-diol (A_2) and tripropargylamine (B_3) with a functional group molar ratio 1:1 under a 25-lb weight for the indicated period on the copper surface is 0.17 ± 0.01 MPa (29), which is 1/97 of the adhesive strength of our system. Even by increasing the number of arms of the monomeric
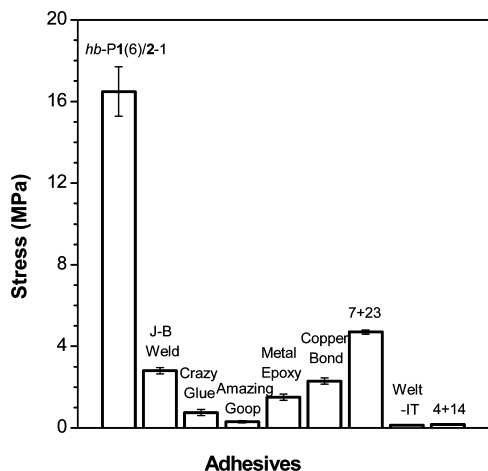
FIGURE 5. Comparison of tensile strength of *hb*-P1(6)/2-1 with commercial adhesives and materials from reference papers on cooper surface. J-B Weld, from J-B Weld, TX; Ace All-Purpose Super Glue (Crazy Glue), distributed by Henkel Consumer Adhesives; Amazing Goop, Electric Product, Pineville, LA; Metal Epoxy, Pacer Technology, Rancho Cucamonga, CA; Copper Bond two-part epoxy (Cooper Bond), The Noble, Grand Haven, MI; 7 + 23, from ref 30; Welt-IT, Devcon, manufactured by ITW Performance Polymers Consumer Division, Riviera Branch, FL; 4 + 14, from ref 29.
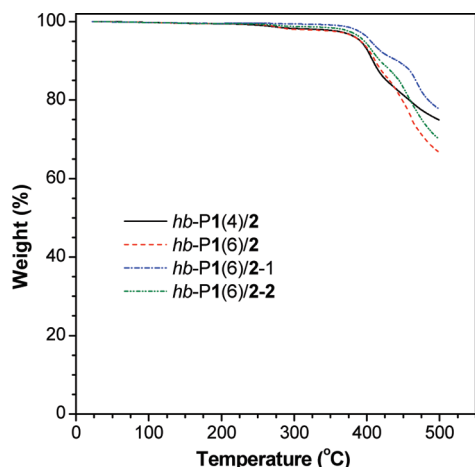

FIGURE 6. TGA thermographs of the hyperbranched poly(triazole)s in air at a heating rate of 20 °C/min.

unit and introducing an amine group, the click polymerized $A_3 + B_4$ approach using N2,N4,N6-tris(3-azidopropyl)-1,3,5-triazine-2,4,6-triamine (A_3) and diprop-2-ynyl 1,2-di(prop-2-ynyl)hydrazine-1,2-dicarboxylate (B_4) with functional group ratio (azide/alkyne) 3:4 at room temperature for 3 days on a copper surface gives an adhesive strength of 4.7 ± 0.1 MPa (30), which is only 2/7 that of our system. Without fully optimizing the conditions, our system already shows a promising result at room temperature for adhesion applications.

Effect of Annealing Temperatures and Time.

Hyperbranched poly(triazole)s are thermally stable under air, as can be seen from Figure 6. No weight loss occurs below 200 °C, and the weight loss is less than 5% at 400 °C for all materials. They are therefore good candidates for high-temperature adhesive applications.

Figure 7 shows the effect of annealing time at 250 °C on lap-shear strength of *hb*-P1(6)/2 prepared by in situ thermal polymerization on the different metal surfaces. With anneal-
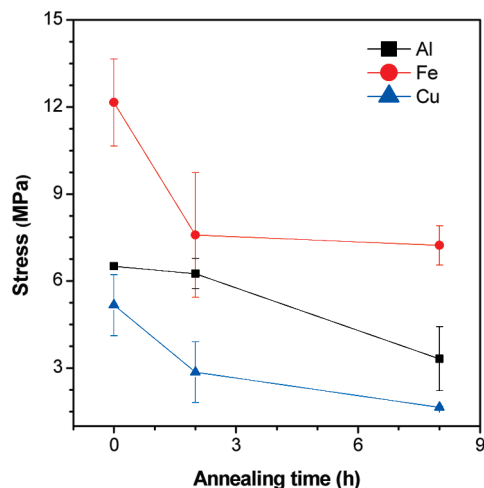

FIGURE 7. Effect of annealing time at 250 °C on lap-shear strength of *hb*-P1(6)/2 prepared by in situ thermal polymerization on different metal surfaces.

ing at high temperature for a sufficient time in air, the adhesive strength decreases on all of the substrates. Compared with the original strengths, the final strength after 2 h annealing for aluminum is 96% of the original strength, for iron it is 62%, and for copper 55%. The final strength after 8 h annealing for aluminum is 51% of the original strength, for iron it is 60%, and for copper 32%. Thermal degradation of small molecules and oligomers, as well as imperfect low molecular weight hyperbranched polymers, contribute to the weight loss. Nevertheless, there is still more than 50% strength left after 2 h annealing at 250 °C on all the substrates.

High temperature annealing after the in situ thermal polymerization of 2 with 1 ($m = 6$) on the different metal surfaces for 8 h at 125 °C was studied in an effort to optimize the process and obtain high adhesive strength. Figure 8 shows tensile strength of (A) *hb*-P1(6)/2-1, (B) *hb*-P1(6)/2-2, and commercial high-temperature adhesives on different substrates. The commercial adhesives fall into the region of our systems, with much lower strength. On an iron surface, tensile strength of the commercial high-temperature epoxies (high-temperature and high-strength epoxy adhesive 4006# and GY-1# high-temperature adhesive) is just 1/7 at 200 °C and 1/3 at 350 °C of tensile strength of our system.

Effect of the Length of Alkyl Chain.

Long flexible alkyl chains have an adverse effect on adhesion strength, but here, in the thermal curing process, the long flexible alkyl chains actually favored adhesion strength (see the Supporting Information, Figure S2, for details). In our previous study, monomer diazide 1 ($m = 4$) and monomer triyne 2 under thermally initiated polycycloaddition gained 64.0% yield with M_w 5500, but with monomer diazide 1 ($m = 6$), gained 75.7% yield with M_w 11 400 (24). A great difference in yielding as well as M_w may be one of the reasons for the difference in adhesion strength between the two kinds of hyperbranched poly(triazole)s on the same metal surface.

Figure 9 shows the strengths of *hb*-P1(6)/2, *hb*-P1(6)/2-1, and *hb*-P1(6)/2-2, prepared by in situ thermal polymerization and annealed at different temperatures (room temperature,
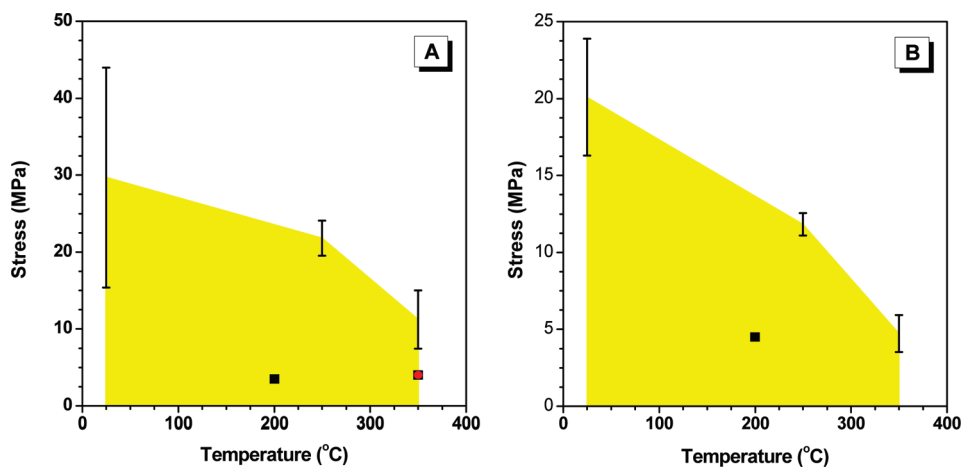
FIGURE 8. Tensile strength of (A) *hb*-P1(6)/2-1,(B) *hb*-P1(6)/2-2 and commercial adhesives (dark square, high-temperature and high-strength epoxy adhesive 4006#, Shenzhen Jinyi Chemical Ltd. Co.; red square, GY-1# high-temperature adhesive, Shenzhen Jinyi Chemical Ltd. Co.) at different temperatures on (A) Fe and (B) Al surfaces.

250, and 350 °C) for 2 h on different metal surfaces. Tensile strength is always higher than lap-shear strength for the same conditions, as reported by other researchers (29, 30). The difference may also be due to the different monomers concentration in the two test modes: the monomer concentration in the tensile mode is approximately 3 times greater than in the lap-shear mode, as shown in Experimental Section. When other conditions are equal, adhesives always have higher adhesive strength on aluminum and iron surfaces than on a copper surface. Also, an excess of monomer **2** on the metal surface always has a higher adhesive strength than that obtained with an excess of monomer **1**. Tof-SIMS technology was performed to understand these phenomena.

Interphase between the Polymer and the Substrate. Interphase is defined as a region that is formed because of bonding and reactions between two materials. It is well-known that polymer interphase plays an important role in functions such as adhesion, protective coating, friction, and wear, microelectronics, and thin film technology. Here, Tof-SIMS was used to check the existence of interphase as well as thickness.

Figure 10 shows negative ion Tof-SIMS depth profiles obtained from aluminum and copper based coating formation with different ratios of monomers after curing. Many ion fragments were obtained (see the Supporting Information, Figure S3 for details). Two kinds of fragments are employed here as characteristic ion fragments to determine the thickness of the interphase layer between the hyperbranched polymer and the metal surface. Ion fragments CN (mass = 26) exist mainly in the polymer and interphase. AlCN (or CuC_2N_2) ion fragments occur mainly in the interphase layer (in the copper substrate, CuC_2N_2 with mass = 115; in the aluminum substrate, AlCN with mass = 53). As seen in Figure 10, the CN ion fragment intensity remains stable at the beginning, and then suddenly decreases with an increase in depth, followed by a smooth decrease to a very low level. These observations mean that with an increase in depth, the ion beam first penetrates the polymer layer, then enters the interphase layer, and finally reaches into the metal substrate. Conversely, of the AlCN (or CuC_2N_2)

ion fragments appears at certain depth, where ion beam reached the interphase, then the intensity gradually increases and exhibits maximum concentration at a certain depth, followed by a stable concentration plateau, and finally dramatically drops to very low level. These observations mean that AlCN (or CuC_2N_2) fragments appear in the interphase, reach maximum intensity at a certain level in the interface, and are sparse in the pure metal substrate. The Tof-SIMS profiles not only provide direct evidence of the existence of an interphase layer between the hyperbranched poly(triazole)s and metal substrates, but also indicate the thickness of the layer on the different metal surfaces with different monomer ratios under the same preparation conditions. It is well-known that the thickness of the interphase has a significant effect on the mechanical strength of an adhesive joint. In general, the strength of the joint increases with increasing thickness of interphase (25). The interphase layer of polymer *hb*-P**1**(6)/**2**-1 with aluminum (approximately 2600 nm) is much thicker than that with copper (approximately 1600 nm). With the same substrate of copper, polymer *hb*-P**1**(6)/**2**-1 has a thicker layer than polymer *hb*-P**1**(6)/**2**-2, though polymer *hb*-P**1**(6)/**2**-2 has a much thicker coating layer (approximately 7000 nm) than polymer *hb*-P**1**(6)/**2**-1 (approximately 2400 nm).

The interphase formed by hyperbranched poly(triazole)s with copper substrate has been explained by Sharpless and co-workers (29). The successful formation of an adhesive on copper surfaces is due to the two crucial features: first, the copper substrate serves as a catalyst for the formation of copper acetylide. Copper(I) species is created by the copper(II) (generated by oxidation of the copper surface) with the copper(0) surface. A low concentration of active Cu(I) is maintained on the surface as the catalyst for reaction. The mechanistic picture of the Cu catalyzed reaction was first proposed by Melda l (8) and Sharpless (9), and was subsequently proved by Sharpless (9, 33). With copper(I), the result is a rate acceleration of 1×10^5 and an absolute regioselectivity of the Cu(I)-catalyzed process. Second, the copper binds to the growing polymer by the interactions of
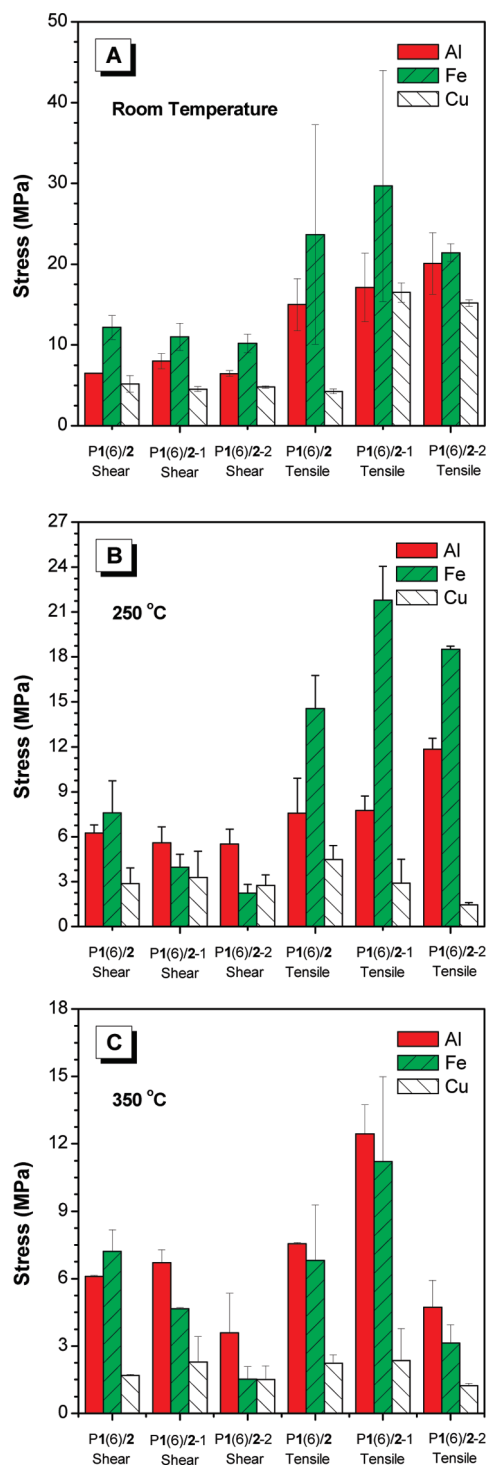
FIGURE 9. *hb*-P1(6)/2, *hb*-P1(6)/2-1, and *hb*-P1(6)/2-2 annealed at (A) room temperature, (B) 250 °C, and (C) 350 °C for 2 h after being prepared by in situ thermal polymerization on different metal surfaces. They were measured by different test modes.

FIGURE 10. Tof-SIMS spectra of hyperbranced poly(triazole)s on different metal surfaces.

pair electrons. Coordination of the basic nitrogen sites to Al^{3+} Lewis acid sites present on Al_2O_3 films on aluminum surfaces occurs. The formation of an oxide layer on aluminum accelerates adhesion. Also the presence of labile N—H hydrogen in the molecule makes possible the interaction with electronegative proton-accepting surface oxide anions.

The high effectiveness of triazoles nitrogen-containing heterocyclic molecules is based on their chelating action and the formation of an insoluble physical diffusion barrier on the oxidized surface of aluminum (Al_2O_3). The formation of strong intermolecular hydrogen bonds and π-interaction between the aromatic rings stabilizes the surface layers produced by the nitrogen heterocyclic molecules (40). Additional stabilization of the protective surface layer formed may be obtained by electrochemical polymerization of heterocyclic molecules on the metal surfaces (41). The thermal stability of the triazole polymer with the aluminum surface was investigated. At low temperatures, only intermolecular hydrogen bonds were observed, which caused no or little adhesive strength exist at low curing temperature on aluminum substrates. With increasing temperature of the sample, the triazole molecules diffused into the Al_2O_3 surface (or pores). Hydrogen bonding of the triazole molecule specifically to isolated Al—OH groups was observed. However, extensive thermal treatment caused decomposition of the triazole, and modes related to the nitrogen ring disappeared (42).

From bond length and binding energy aspects, the binding energies of Al—N are in the range of 2.78—3.54 eV/atom, with the bond length approximately 0.18 nm calculated by using local spin-density approximation and generalized gradient approximation (43). The Cu—N bond length is about 0.20 nm (44, 45), and the binding energies are approximately 1.45 —2.09 eV/atom (46). The differences in binding energy and bond length between aluminum and copper binding with nitrogen cause different adhesive strengths macroscopically as shown by mechanical test, if the failure occurs within the interphase layer.

the surface with multiple triazoles and also dangling alkynes in σ- or π-interactions.

Stable complexes between aluminum and nitrogen-containing heterocyclic molecules have been reported previously (33, 38, 39). Aluminum surfaces are covered with oxide layers having an inner dense and an outer permeable layer. These molecules are electron-rich nucleophiles, able to interact with the surface through the nitrogen atom lone-
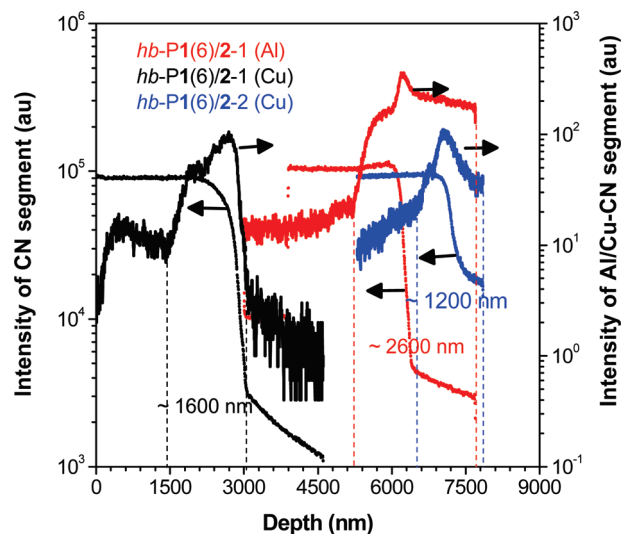
ACS **APPLIED** MATERIALS
&INTERFACES

FIGURE 11. *hb*-P**1**(6)/**2** taken under UV irradiation after (A) tensile and (B) lap-shear tests. The polymer was annealed at 250 °C for 2 h before the experiment in B.

Failure Mechanism Observation. In a previous study (24), we found that these hyperbranched poly(triazole)s are light-emitting materials. Fluorescence can be generated by UV light. Here, we used this property to check the coverage of the in situ polymerized adhesive polymers on the substrate surfaces as well as the failure mode cause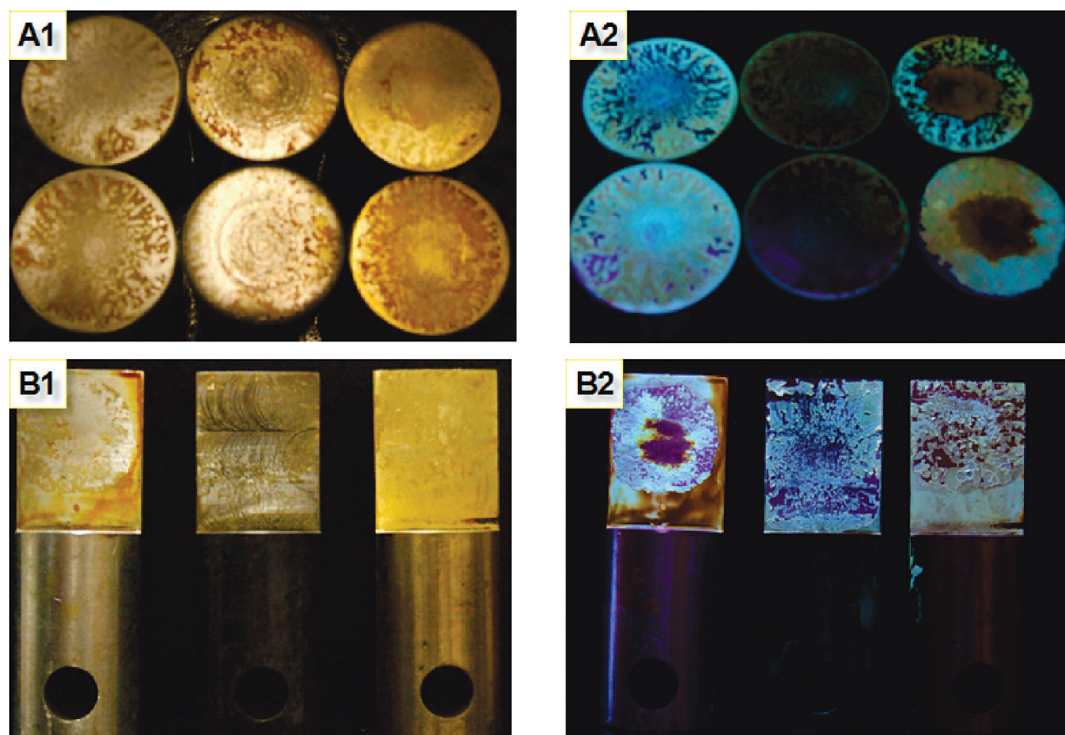d during mechanical testing. The photographs in Figure 11 show *hb*-P**1**(6)/**2** taken under UV irradiation after (A) tensile and (B) lap-shear tests. The polymer was annealed at 250 °C for 2 h before the experiment in Figure 11B. In the successful experiments, the in situ polymerized polymers covered the entire testing surface to yield an accurate result; otherwise, underestimation would occur. With the usage of UV light, obvious and easy observation is possible. The failure mode detected by UV irradiation shows that in all successful tests, fracture occurred inside the polymers as well as between the polymer and metal surface, as Figure 11A2, B2 indicate. The combination failure mode of adhesive failure and interface failure is the failure mode for our systems with metal substrates.

CONCLUSIONS

In this work, we used in situ click polymerization of azide/alkyne through an effective $A_2 + B_3$ route to obtain hyperbranched poly(triazole)s with effective adhesive strength in both tensile and lap-shear modes on metal substrates at room temperature and elevated temperatures. The effects of curing kinetics, annealing temperature and time, catalyst, alkyl chain length in diazide **1** monomer, metal substrate, azide/alkyne molar ratio, and test mode were addressed to improve the adhesion strength. Our system displays approximately two orders greater adhesive strength than other systems with a similar preparation method using the azide/alkyne click reaction ($A_2 + B_3$ mode) on a copper surface at room temperature. Our system also has much higher adhesive strength than commonly used commercial adhesives at room temperature (55−127 times higher) as well as at elevated temperatures (3−7 times higher). The interphase between the hyperbranched poly(triazole)s and substrates was characterized qualitatively and quantitatively. The thickness of interphase, as well as the substrate composition, is critical to the adhesion strength with thicker interphase (excess of triyne 2 monomer) and the higher binding energy between polymer atoms and substrate atoms (e.g., aluminum substrate) generating higher bonding strength. The unique light-emitting property of the polymers under UV irradiation provides an easy and clear way to detect failure modes of adhesion under mechanical tests.

Supporting Information Available: Detailed information is available for magnitudes with standard deviations on the effects of curing time, curing temperature, catalysts, annealing time, annealing temperature for the different hyperbranched poly(triazole)s (*hb*-P**1**(4)/**2**, *hb*-P**1**(6)/**2**, *hb*-P**1**(6)/**2**-1, and *hb*-P**1**(6)/**2**-2) on the different metal substrates (iron, aluminum, and copper) with different adhesive strengths (lap-shear and tensile), listed in tables and partially plotted in graphs; effect of alkyl chain length on adhesive strength of *hb*-P**1**(*m*)/**2** at different temperatures prepared by in situ thermal polymerization on the different metal surfaces; total ion fragment content of depth profiles on Tof-SIMS of

hyperbranched polymers hb-P**1**(6)/**2**-1 and hb-P**1**(6)/**2**-2 on Cu and Al metal surfaces (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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