Synthesis of Triazole-functionalized Phenolic Resin and its Inherent Flame Retardant Property

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A novel triazole-functionalized phenolic resin was developed, and its thermal and flame-retardant properties were investigated. The triazole group was incorporated as a pendant unit on the phenolic resin *via* copper-mediated click chemistry between propargylated phenolic resin and benzyl azide. The newly-developed triazole-functionalized phenolic resin showed higher thermal stability and char yield, together with a reduced total heat release (THR), than the non-functionalized bare phenolic resin, indicating enhanced flame retardancy for the triazole-functionalized phenolic resin.

Key Words : Phenolic resin, Flame-retardant polymer, Char yield, Thermal properties, Triazole

Introduction

Phenolic resins and their composites have been widely used for many years in various contexts, ranging from construction materials to the technology and aerospace industries. They have several desirable characteristics, including high thermal resistance, dimensional stability, flame retardance and superior mechanical and ablative properties.[1,2]

Phenolic resins are generally prepared by reactions between formaldehyde and phenol in the presence of acid or base. When prepared by acid catalysis, they are normally called novolac-type resins. In these resins, the molar ratio of formaldehyde to phenol is less than 1, and substitution occurs mostly at the ortho position of the phenol. In contrast, base-catalyzed pathways produce more cross-linked structures, and are called resole-type phenolic resins, with substitutions at both ortho- and para-positions.

Phenolic resins with improved thermal and pyrolysis characteristics are desirable for producing composites for thermo-structural applications.[3,4] Although conventional phenolic resins are already considered to be temperature-resistant polymers and are currently in use for the above-mentioned applications, some of the properties of phenolic resins need further improvement for meeting the ever-increasing performance requirements.

With sufficient heat and oxygen, most organic polymers will burn. Fundamentally, four processes are involved in the polymer combustion cycle: heating, decomposition, ignition, and combustion. In order to increase its flame resistance, the polymer system should function to interrupt this cycle.[5] A polymer system that produces flame inhibitors, such as carbon dioxide, water vapor, hydrogen halides and/or nitrogen, can also interrupt the cycle. Carbon dioxide and water vapor not only protect the burning polymer from contact with oxygen but also remove heat from the burning polymer.[6] Halogenated polymers are generally highly flame resistant because they produce hydrogen halides, which are efficient scavengers of H and OH radicals in the flame region.[7] Nitrogen-generating flame-retarding polymers have certain advantages over other flame-retarding polymers due to their low production of smoke and of toxic combustion compounds.[8]

Recently, triazole has been reported to release nitrogen gas during decomposition, and incorporating triazole into the bisphenol polymer can significantly enhance this polymer's thermal stability and flame retardancy.[9]

We adapted this concept to develop a new class of inherently flame retardant phenolic resins by incorporating triazole as a pendant unit on the phenolic resin *via* copper-mediated click chemistry. The newly developed triazole-functionalized phenolic resin showed higher thermal stability and char yield, together with a reduced total heat release (THR), than did the non-functionalized (bare) phenolic resin, indicating enhanced flame retardancy for the triazole-functionalized phenolic resin.

Experimental

Materials. Phenol and formaldehyde were purchased from Samchun Chemicals. Propargyl bromide and benzyl bromide were purchased from Sigma Aldrich. All other chemicals were obtained from commercial sources and used without further purification.

Characterization. ^{1}H NMR spectra were obtained on an Agilent 400-MR (400 MHz) instrument using acetone-d_6 or DMF-d_7 as a reference or internal deuterium lock. FT-IR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer.

TGA was carried out with a TA2410 thermogravimetric analyzer. The TGA curves were obtained at a scanning rate of 10 °C/min.

Heat release rate and total heat release data were measured from Cone Calorimeter at a heat flux of 50 kW/m^2 according to ISO 5660-1 standard.

Synthesis of Novolac-type Phenolic Resin 1. To a mixture of phenol (17 g, 0.18 mol) and formalin (37 wt % formaldehyde, 9.66 mL, 0.12 mol) at 50 °C, 1 mL of 1 M HCl was added. The mixture was then stirred at 95 °C for 90 min. The crude product was washed with hot distilled water to remove any unreacted phenol, formaldehyde, and catalyst. Water was then removed to obtain a pale yellow novolac-type phenolic resin. Yield = 97%; δ_H (400 MHz, acetone-d_6) 7.0-6.6 (4H, br signal, Ar*H*), 3.9-3.5 (2H, br signal, methylene C*H*$_2$); (KBr)/cm^{-1} 3400, 3033, 2929, 1602.

Propargylation of Novolac-type Phenolic Resin 4. Phenolic resin **1** (19 g, 0.17 mol) was dissolved in 20 mL of dimethyl formamide at room temperature under agitation, and NaOH (5 g, 0.12 mol) was added in portion to form a purple solution. Propargyl bromide (15 g, 0.12 mol) was then added dropwise at intervals of 30 min. The mixture was heated to 50-60 °C and maintained at this temperature for 3 h until it turned to a pale yellow solution and formed KBr

salt. After filtration of the residual salt and the excess propargyl bromide was evaporated *in vacuo* to give the product **4**. This was used for the next reaction without further
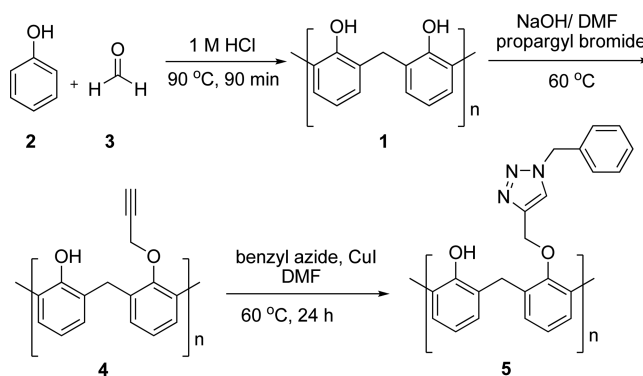
Scheme 1. Synthesis of the novolac-type phenolic resin **1**, its propargyl ether **4** and the triazole ether derivative **5**.
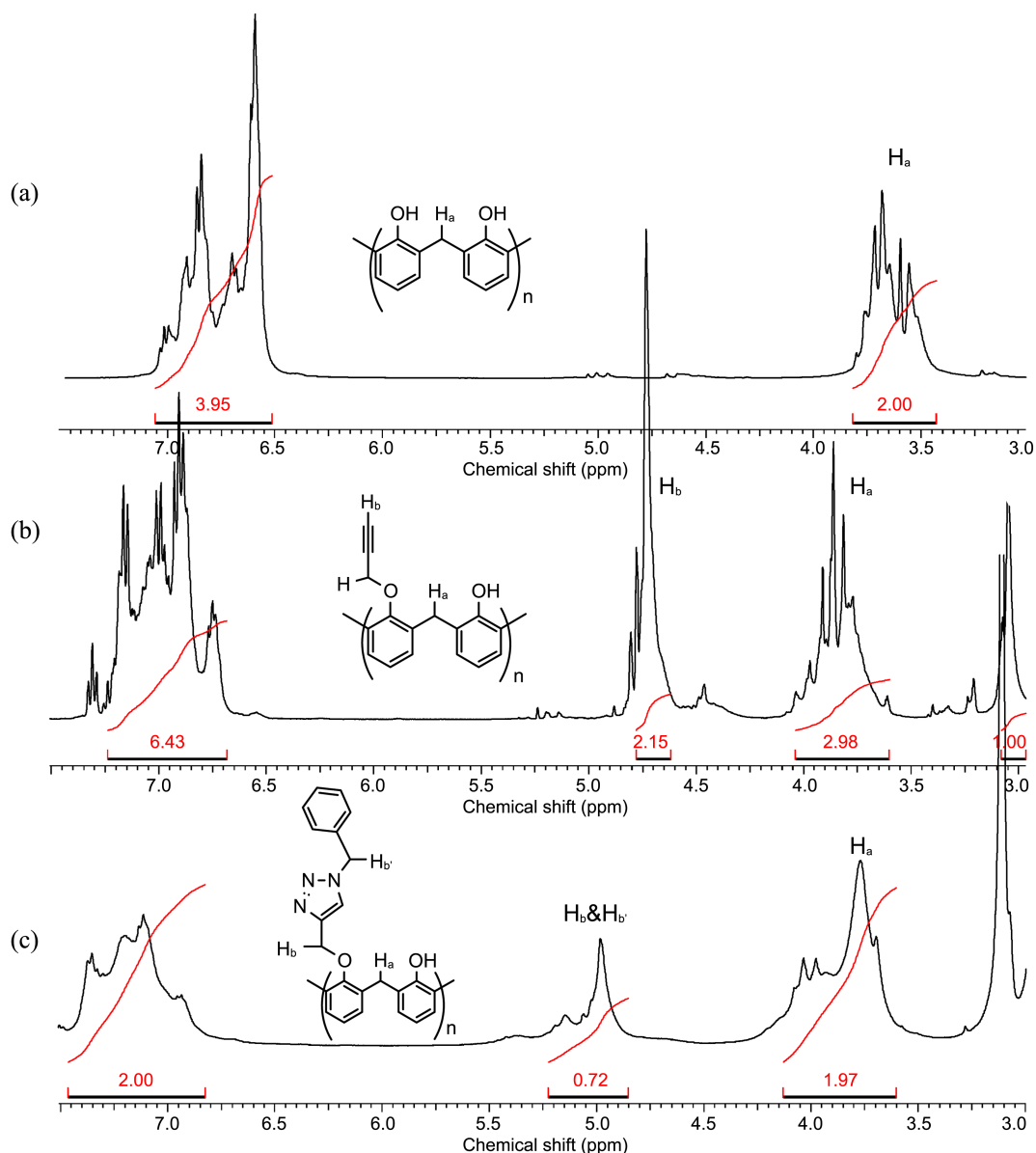
Figure 1. ^{1}H NMR spectra of the phenolic resin **1** (a), its propargyl ether derivative **4** (b) and triazole-functionalized phenolic resin **5** (c).

purification. δ_H (400 MHz, acetone-d_6) 7.3-6.6 (6H, br signal, Ar*H*), 4.7-4.5 (2H, br signal, OC*H$_2$*CC), 3.9-3.5 (3H, br signal, methylene *CH$_2$*), 3.1 (1H, br signal, C*CH*); (KBr)/ cm^{-1} 3400, 3288, 3100, 3033, 2122.
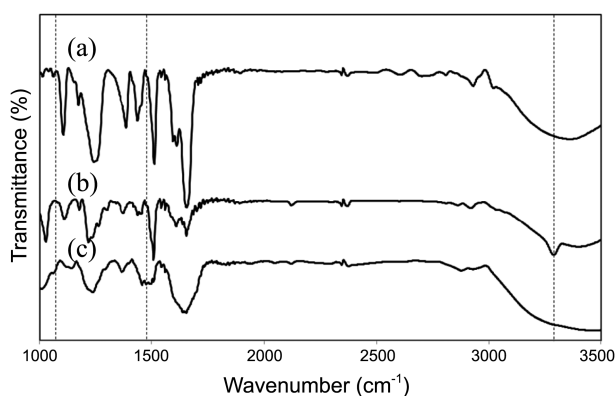
Triazole-functionalized Phenolic Resin 5. The propargyl-functionalized phenolic resin **4** (6 g, 0.05 mol) was added to the benzyl azide solution, prepared by stirring 5 g of benzyl bromide and 2.5 g of sodium azide for 10 min, in dimethyle formamide. To this reaction mixture, a catalytic amount of copper(I) iodide (250 mg, 0.05 wt % of azide) was added and the solution was stirred for 30 min at rt. After comple-tion of the reaction, the copper(I) iodide and residual sodium bromide were filtered out, and the crude product was precipitated into water and the precipitate was dried under high vaccum overnight to give the triazole-functionalized phenolic resin **5** (5.4 g, 90% yield) as a dark bown solid. δ_H (400 MHz, DMF-d_7) 7.5-6.7 (2H, br signal, Ar*H*), 5.4-4.9 (1H, br signal, C*H$_2$*O), 4.1-3.5 (2H, br signal, methylene *CH$_2$*); (KBr)/cm^{-1} 3400, 3033, 1475, 1035.

Results and Discussion

Synthesis of a Novolac-type Phenolic Resin and its Pro-pargyl Ether Derivative. A novolac-type phenolic resin **1** (See Scheme 1) was first prepared by the reaction between phenol **2** and formaldehyde **3** (1:0.7 by mol) in the presence of hydrogen chloride at 90 °C for 90 min. The hydroxyl groups of the phenolic resin **1** were then propargylated by reaction with propargyl bromide in the presence of sodium hydroxide to give the propargyl ether derivative **4** (Scheme 1).

The degree of propargylation was estimated by comparing the integral of the bridged methylene peak (-CH$_2$-) at 3.6 ppm to that of the terminal alkyne proton at 4.7 ppm in **4** in the ^{1}H NMR spectra, and was found to be 73% (Figure 1). This polymer was used for next reaction without further purification.

Triazole Formation *via* Click Chemistry. The propargyl group in **4** was further transformed into the triazole to produce the desired triazole-functionalized phenolic resin **5** (Scheme 1). The triazole formation was carried out *via* click

Figure 2. FT-IR spectra of the phenolic resin **1** (a), its propargyl ether derivative **4** (b), and triazole-functionalized phenolic resin **5** (c).
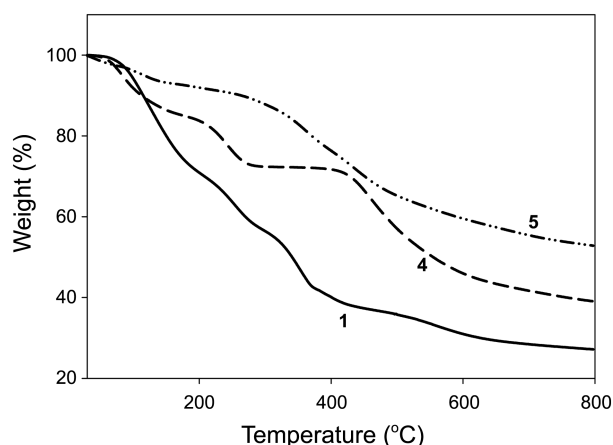
Figure 3. TGA diagrams of the phenolic resin (bold curve), its propargylated ether derivative (long-dashed curve), and the tri-azole-functionalized phenolic resin (alternating dashed and dotted curve).

chemistry using benzyl azide and a catalytic amount of copper (I) iodide.[9,10] The cycloaddition between azide and alkyne in the presence of copper catalyst is a well-establish-ed chemistry for the formation of triazole,[10] and the conver-sion was confirmed by comparative IR spectroscopy (Figure 2): the strong peak corresponding to the terminal alkyne (-C≡C–H), at 3100 cm^{-1} for **4**, almost disappeared for the triazole-functionalized phenolic resin **5**, and a new peak corresponding to triazole ring stretching vibrations appeared at 1475 and 1035 cm^{-1} for **5**, indicating a successful conver-sion of the alkyne to the triazole group.[9]

Thermo Gravimetric Analysis (TGA). The thermal behaviors of the three phenolic resins (**1**, **4** and **5**) were analyzed by TGA. As shown in Figure 3 and Table 1, the decomposition temperature of the triazole-functionalized phenolic resin **5** was much higher than those of the non-functionalized phenolic resin **1** and its propargyl ether derivative **4**, indicating that the triazole functionalization, indeed, improved the thermal stability of the phenolic resin. In addition, considerably more char was observed at 800 °C for the triazole-functionalized phenolic resin **5** than for the propargylated phenolic resin **4** and for the bare phenolic resin **1**, suggesting that the triazole-functionalized phenolic resin **5** can produce the lowest amounts of combustible gases among all three phenolic resins tested, and suggesting that the triazole-functionalization might enhance the flame retar-dancy of the phenolic resin.

Cone Calorimeter Experiment. To determine the heat release of the novel triazole-functionalized phenolic resin **5**, cone calorimeter experiments were carried out according to

Table 1. Thermal behavior of three phenolic resins (**1**, **4** and **5**)

Phenolic resin	10% Degradation (°C)	20% Degradation (°C)	Char yield at 800 °C (%)
1	114	149	27.2
4	112	230	39.1
5	263	370	52.8

(a)

(b)
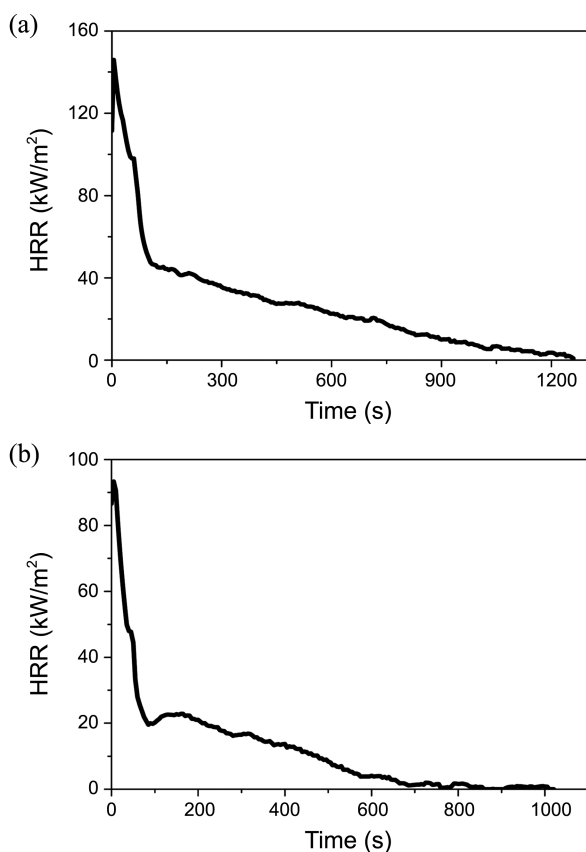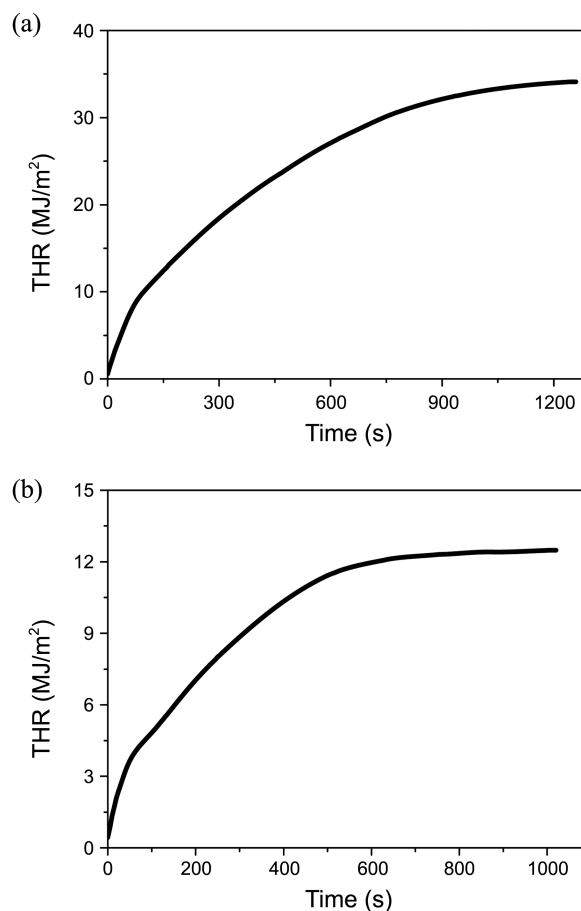

Figure 4. Heat release rate (HRR) diagram of the bare phenolic resin **1** (a) and the triazole-functionalized phenolic resin **5** (b).

(a)

(b)

Figure 5. Total heat release (THR) diagram of the bare phenolic resin **1** (a) and the triazole-functionalized phenolic resin **5** (b).

ISO-5660-1 standard with a heat flux of 50 kW/m^2. Cone calorimeter experiments are effective tools in determining the flammability of any flammable material. These experiments can measure the amounts of heat released by the time of combustion: an effective flame retardant system shows a low heat release rate by the time of combustion.[11] It was found that the heat release rate (HRR) of the triazole-functionalized phenolic resin **5** was much lower than that of the novolac-type bare phenolic resin **1** (93.33 kW/m^2 for **5** and 146.02 kW/m^2 for **1** at t = 0 in Figure 4), indicating the enhanced flame-retarding nature for the triazole-functionalized phenolic resin.

Also, Figure 5 shows the total heat release (THR) of the phenolic resin and triazole-functionalized phenolic resin, with the slope of these curves indicating time of fire spread. The maximum THR for the bare phenolic resin **1** was determined to be about 35 mJ/m^2, and a much lower value of *ca.* 13 mJ/m^2 was obtained for the triazole-functionalized phenolic resin **5**, indicating that the triazole-functionalized phenolic resin **5** produces less flammable combustion products than does the bare phenolic resin **1**. These results are consistent with the char formation data obtained by the thermo gravimetric analyses.

Conclusions

In conclusion, we have successfully developed a triazole-functionalized phenolic resin **5**, and investigated its thermal and flame-retardant properties. The newly-developed triazole-functionalized phenolic resin showed much higher thermal stability and char yield, as well as much lower heat release and smoke production than the corresponding non-functionalized bare phenolic resin. We believe that the incorporation of triazole into the phenolic resin would meet the ever-increasing performance requirements for this industrially important polymer.

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