Addition-Curable Propargyl-Containing Novolac-Type Phenolic Resin: Its Synthesis, Characterization, Cure, and Thermal Properties

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ABSTRACT: In this article, propargyl functionalized novolac resins (PN resins), with varying propargyl contents and varying molecular weights, were synthesized conveniently. The structural characteristics were determined by ^{1}HNMR and FTIR methods. Thermal cure studies revealed that the uncatalyzed thermal cure was remarkably affected by propargyl extent, while it was hardly affected by molecular weight. The processability of the as-prepared PN resins was excellent as matrix of composite materials. The cure mechanism was complicated; postcure at high temperature was required to achieve entire crosslink formation. Both dynamic mechanical analysis and thermogravimetric analysis showed that the cured PN resins had substantially improved thermal mechanical properties and thermal stability in comparison to conventional cured phenolics. High propargyl extent was preferred for high thermal stability. The results show that PN resin is one of the ideal candidates for advanced composites matrices in thermostructural and ablative applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1010–1017, 2006

Key words: thermosets; modification; curing of polymers; thermal properties

INTRODUCTION

Phenolic resins and their composites have been widely used for many years in various applications, from commodity construction materials to high technology aerospace industries. Phenolic resins are considered to have several desirable characteristics, such as thermal resistance, dimensional stability, flame retardance, and superior mechanical and ablative properties.[1,2] But conventional phenolics should be cured via condensation at high temperatures with the evolution of volatiles, which necessitates the application of pressure during compression molding and makes them unsuitable for resin transfer mold (RTM) process. Limited shelf life and inherent brittleness are the major shortcomings. Furthermore, the cured materials have low thermo-oxidative stability. To solve these problems and to meet the ever-increased performance and novel processes (such as RTM requirements), it is necessary to functionalize phenolics with proper active groups, to make them crosslinkable via addition mechanism instead of condensation.[3] The general approach for designing such novel thermoset is to anchor thermally stable addition-curable groups onto the backbone of novolac and to induce their addition polymerization during processing.[4]

Novolac resins modified by allyl groups,[3,5,6] maleimide groups,[7,8] phenyl ethynyl groups,[9,10] epoxy groups,[11,12] benzoxazoline structure,[13,14] benzoxazine structure,[15,16] phenol–triazine structure,[17,18] ethynyl phenyl azo groups,[19] and propargyl groups[20,21] have been reported. These nonconventional phenolic resins cure principally via addition polymerization.

Reghunadhan Nair C. P. had synthesized propargyl functionalized novolac resins (PN resins) and characterized their structural and processing properties. The results showed that PN resins were ideal matrices for composite materials.[20,21] But systematic research on PN resins has been scarce. In view of this, the present article focuses on facile synthesis, structural characterization, and cure processablity of this type of phenolic resin. Thermal properties of the cured PN resins are also studied.

EXPERIMENTAL

Materials

Phenol(A.R., Beijing Yili Chemicals Factory, China), formalin (A.R., 36–40% aqueous solution, Jinan Shengquan Chemicals Company, China), oxalic acid (A.R., Beijing Chemical Reagents Corp., China), potassium hydroxide (A.R., Tianjin Zonghengxing Chemi-

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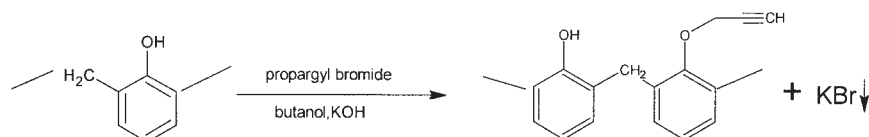
Scheme 1 Synthesis of PN resin.

cals Corp., China), and butanol (A.R., Beijing Yili Chemicals Factory, China) were used as received. propargyl bromide (A.R., Yangzhou Yangnong Chemicals Corp. Ltd., China) was distilled before use.

Instruments

FTIR spectra were recorded with Perkin–Elmer IR2000 spectrometer. Differential scanning calorimetry (DSC) was performed on Mettler–Toledo DSC822^e, at a heating rate of 10°C/min and a N_2 purge rate of 50 mL/min. Solution for ^{1}HNMR spectra were run on Bruker AV400, with DMSO-d_6 as solvent and TMS as internal standard. Dynamic mechanical analysis (DMA) of the resins were determined by PE DMA7, using compression mode, at a heating rate of 5°C/min and a frequency of 1 Hz. Thermal stability was evaluated by TGA on Netzsch STA409PC, at a heating rate of 10°C/min, and by DMA on Netzsch DMA242C, at a heating rate of 5°C/min in N_2 flow. Viscosity of resin melts was determined using NDJ-79 rotating viscometer.

Synthesis of novolac resins

In a typical synthesis, to a mixture of phenol (94 g, 1 mol) and formalin (37 wt % formaldehyde, 25.5 g, 0.85 mol) at 50°C, oxalic acid (2 g, about 2 wt % of phenol) was added. The mixture was stirred at 85°C for an appropriate time, and the condensation reaction was stopped by neutralization with aqueous KOH solution (0.1 mol/L). The crude product was washed with hot distilled water at 90°C to remove the unreacted phenol, formaldehyde, and catalyst, and then, water was removed by rotary evaporation to obtain a pale yellow transparent novolac resin. Yield was 95.7%. Novolac resins with varying average molecular weights were prepared by neutralizing at different refractive indexes of the reaction system. They were characterized by FTIR and ^{1}HNMR techniques.

Synthesis of PN resins

In a typical synthesis, novolac (104 g, 1 mol) was dissolved in 120 g butanol at 50°C under agitation, and then KOH (53.3 g, 0.8 mol) was added in batches to form a purple solution. To the aforementioned solution, propargyl bromide (95.2 g, 0.08 mol) was added dropwise in intervals of 30 min. The mixture

was heated to 65°C and maintained at this temperature for 3 h till it turned to be pale yellow and was then filled with KBr. After filtration, residual salt in butanol was washed away by hot distilled water. The butanol solution was rotary evaporated to give a viscous transparent brown-red resin. Thus, PN resin with a propargyl content of 80% was prepared.

Yield is 91.7%. IR (KBr) cm^{-1}: 3400 (—OH), 3288 ($\equiv$C—H), 3033 (aromatic C—H), 2122 (C$\equiv$C); ^{1}HNMR (DMSO) δ: 3.35–3.53 ($\equiv$C—H), 3.70–3.81 (-φ—CH_2—φ-), 4.7–4.8 (—OCH_2C$\equiv$C—), 6.6–7.3 (aromatic hydrogen).

Element analysis showed that the residue of bromine in PN resins was undetectable. PN resins with varying propargyl contents or with varying molecular weights were also prepared as per the same procedure described earlier.

Thermal cure of PN resins

PN resins were cured as per the following protocol:
R.T.→@150 °C for 1 h→@170 °C for1 h →@190 °C for 2 h →@210 °C for 3 h →@230 °C for 1 h →@250 °C for 2 h

In some cases, postcure at 280°C was provided.

TABLE I
Optimization of the Reaction Parameters in the Synthesis of PN

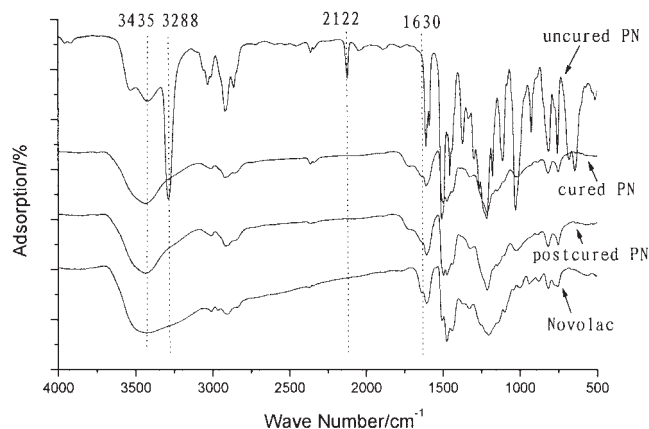| Reaction time (h)	pH value
At 60°C	
0.5	11
1	9.5
1.5	8
2	7
3	6
At 65°C	
0.5	10
1	8
1.5	7
2	6
3	6
At 75°C	
0.5	9.5
1	7
1.5	6
2	6
3	6

Figure 1 FTIR spectra. (KBr)

The completion of the cure was monitored by FTIR spectra and DSC analysis.[20,21]

RESULTS AND DISCUSSION

Optimization of synthesis parameters

PN resins were prepared by Williamson etherification reaction (Scheme 1). With the proceeding of the reaction, pH value of the reaction mixture changed gradually from about 11 to 6.5. So, the reaction parameters were optimized by measuring pH value of the reaction mixture at different time intervals. The results are shown in Table I.

To avoid the evaporation of propargyl, the reaction temperature should not be higher than the boiling point of propargyl bromide (b.p., 80°C). From the results in Table I, the ideal reaction parameter is determined as at 65°C and for 2 h.

The present synthetic procedure has advantages over the literature methods[22,23] in three aspects: first, butanol, which was less toxic and easy to remove, was used as solvent instead of DMF; second, because of the good solubility of alkali and propargyl bromide in butanol, the reaction system was homogeneous, thus, the reaction time could be shortened; third, purification was remarkably simpler.

Characterization of typical PN resin

In the synthesis, by tuning the concentration of alkali and propargyl bromide, the degree of propargyl etherification was easily controlled. The structure of the as-prepared PN resins was characterized by ^{1}HNMR and FTIR. In ^{1}HNMR spectra of a typical PN resin, signals at 3.4 ppm were due to $-C{\equiv}CH$, while that at 4.4–4.6 were due to $-OCH_2C{\equiv}C-$ and at 4.3–4.4 were due to $-\varphi CH_2C{\equiv}C-$. Signals at 6.7–7.2 were naturally due to aromatic protons and bridged $-CH_2-$ appeared at 3.4–3.6 as a broad peak. FTIR of PN resin given in Figure 1 showed the characteristic absorption of ${\equiv}C-H$ bond at 3272 cm^{-1} (stretching vibration, strong) and $C{\equiv}C$ bond at 2120 cm^{-1} (stretching vibration, weak), and the absorption of phenolic hydroxyl group at 3450 cm^{-1} (weakened remarkably compared to that of the corresponding Novolac precursor).

The propargyl content was calculated[24] from the results of ^{1}HNMR for PN resin and its Novolac precursor. The equations are given as follows:

$$\text{Propargyl content (\%)} = A_1(n+3)/(A_2(n+4)) \tag{1}$$

$$n = (4A_4 - A_3)/(A_3 - 1.5A_4) \tag{2}$$

where n is the average polymerization degree, A_1 is the integral of methylenic hydrogen of propargyl group in PN resin, A_2 is the integral of methylenic hydrogen of bridged methylene in PN resin, A_3 is the integral of aromatic hydrogen in novolac resin, A_4 is
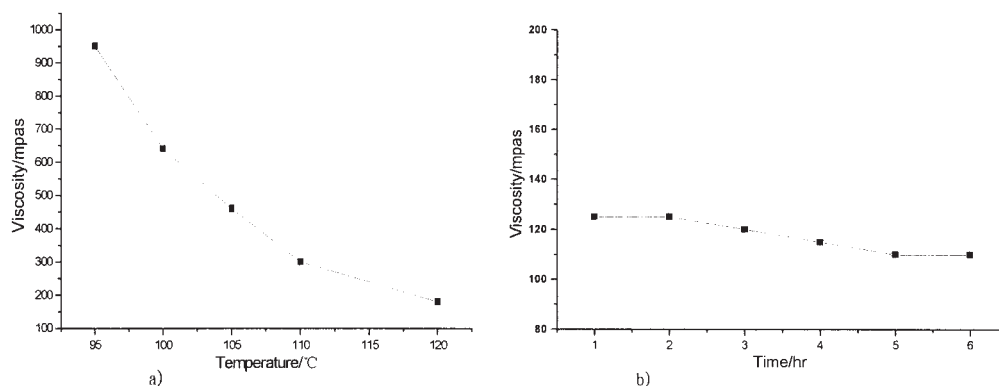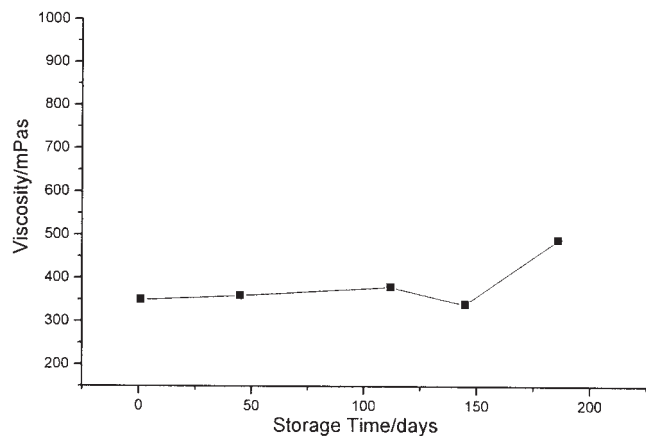

Figure 2 Viscosity–temperature and viscosity–time relationships of PN by NDJ-79 rotating viscometer. In (a) samples were dwelled at each temperature for 1 h; In (b) samples were measured at 110°C.

Figure 3 Shelf life of PN resin. Samples were dwelled at 110°C for 2 h, before measurement; PN resin was stored under natural conditions.

Figure 4 DSC profile of a typical PN resin. (Heating rate, 10°C/min; N_2 purging rate, 50 mL/min.)

the integral of methylenic hydrogen of bridged methylene in novolac resin.

PN resins with varying propargyl contents of 40, 65, 72, 90, and 100% were prepared. PN resin with propargyl content of 90% was taken as an example to characterize its structure.

Processability of PN resins

PN resin is soluble in common organic solvents, such as acetone, THF and DMF. The molecular weights have a dominant effect on the phase states of PN resins at ambient temperature; with increase in molecular weight, PN resins turn from viscous fluid to soft gel and then to solid. For PN resins derived from novolac of a certain molecular weight, the viscosity decreases with increase in propargyl content. When the molecular weight of the novolac is proper, the corresponding PN is a viscous resin at ambient temperature. These make it suitable for preparation of fiber prepregs for fabrication of advanced composite materials.
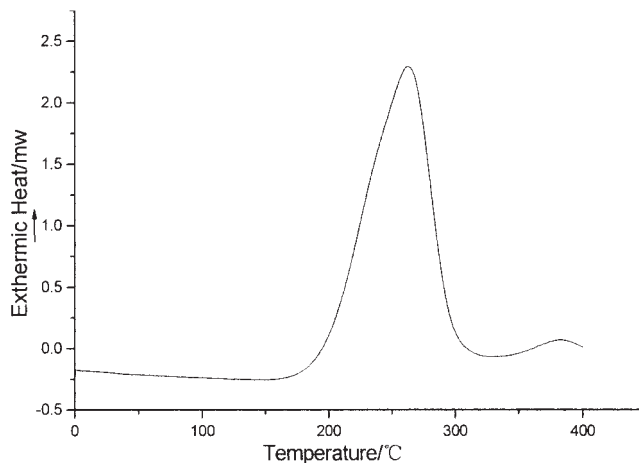
The structure of PN resin can be tailored easily, to fulfill the requirements of various material processes. Here PN-1, in Table II, was taken as an example to investigate its rheology and its shelf life. Experimental data are plotted in Figures 2 and 3.

Figure 2 revealed that PN resin was suitable for RTM technique. However, the conventional phenolic resins could not be processed by this advanced technique.

The plot in Figure 3 implied that the shelf life of PN was long enough, and it was easy to store. This makes PN resin superior to conventional thermosetting phenol–formaldehyde resins.

Thermal cure of PN resins

PN resins can undergo cure via addition reaction of ethynyl groups, either linearly or in a cyclic way, by

different crosslinking mechanisms.[25,26] In view of thermal stability, catalyzed cyclotrimerization is preferred to thermal or linear polymerization. However, a suitable catalyst to cyclotrimerize PN is difficult to find.[27–30] Uncatalyzed thermal cure of various PN resins was studied here.

As shown in Figure 4, a single typical exotherm from 170 to 300°C, with a peak temperature at about 262°C, is observed in DSC profile of PN resin.

The effects of propargyl content and molecular weight on thermal cure of PN resins were investigated. Table II summarized the DSC data of PN resins with varying propargyl contents, while Table III summarized the DSC data of PN resins with varying molecular weights.

Evidenced from Table II, the cure exothermic enthalpy (ΔH) nearly increased linearly with increase in propargyl content. The peak temperature remained constant, but the onset temperature was a bit lower for a higher propargyl content, which implied the effect of concentration during thermal cure.

TABLE II
Cure Characteristics of PN Resins with Varying Propargyl Contents[a]

Systems[b]	Propargyl extent (%)	T_1^c (°C)	T_2^d (°C)	T_3^e (°C)	ΔH (J/g)
PN-1	90	202	263.9	288	822
PN-2	65	208	264.8	290.6	620
PN-3	40	219	263	297.4	343

[a] Molecular weight, 578; heating rate, 10°C/min; N_2 flow rate, 50mL/min.
[b] All the PN resins derive from the same novolac precursor.
[c] Onset temperature of cure exotherm.
[d] Peak temperature of cure exotherm.
[e] Endset temperature of cure exotherm.

TABLE III
Cure Characteristics of PN resins with Varying Molecular Weights[a]

Systems[b]	Novolac precursor M_n (g/mol)	T_1[c] (°C)	T_2[d] (°C)	T_3[e] (°C)	ΔH (J/g)
PN-4	421	201	263	295	818
PN-5	578	196	262	296	781
PN-6	767	196	260	293	774
PN-7	851	208	260	292	657
PN-8	981	198	260	295	714

[a] Propargyl extent, 72%; heating rate, 10°C/min; N_2 flow rate, 50mL/min.
[b] Here the PN resins have the same propargyl content of 76% (by ^{1}HNMR).
[c] Onset temperature of the cure exotherm.
[d] Peak temperature of the cure exotherm.
[e] Endset temperature of the cure exotherm.
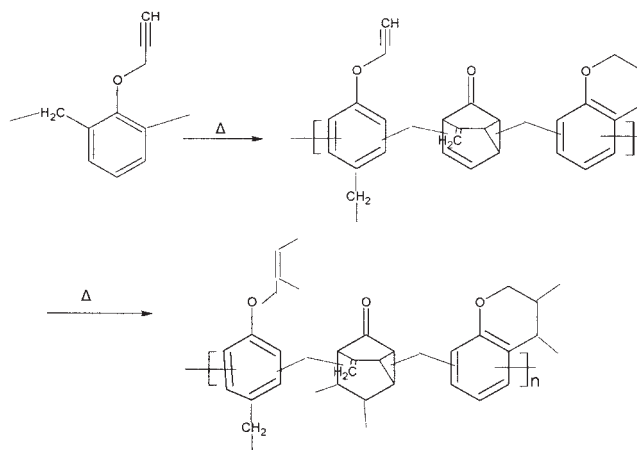

Scheme 2 Possible cure mechanism for PN.[20,21]

When the molecular weight of PN varied, the cure characteristics were almost identical. The molecular weight had little effect on cure behaviors of PN resins. This may be attributed to the same concentration of propargyl groups for these PN resins. It implied that there was no apparent relationship between phenolic backbone and thermal cure, and the curing exotherm of PN resins mainly resulted from the polymerization of propargyl groups.

However, thermal cure mechanism is still obscure because of the numerous ways in which polymerization can proceed, combined with the fact that only few characterization techniques are available to study these complex thermoset structures.

William.E. Douglas reported uncatalysed thermal cure reactions of propargyl ether-terminated bisphenol-A (PBA).[27] DSC, FTIR, ^{1}HNMR, and ^{13}CNMR analysis of the contents from partially cured PBA showed that thermal cure involves prior sigmatropic rearrangement of propargyl groups to 2H-1-benzopyran structure which subsequently polymerize.

R.L. Bindu presented a possible cure mechanism for PN resin.[20,21,31,32] Phenol propargyl ethers with at least one free ortho position rearrange to 2-H chromene; when both ortho positions are occupied, the arrangement results in cyclic diene ketone. These two rearranged structures can be cured through double bonds. When both ortho and para positions are substituted, the rearrangement does not occur and the propargyl groups polymerize linearly. The postulated mechanism is shown in Scheme 2.

According to the aforementioned hypothesis, the amount of unetherified phenolic hydroxyl groups will remain unchanged and ethylene bonds should disappear in the cured PN resin. But in Figure 1, the absorbency of phenolic hydroxyl groups at 3300–3500 cm^{-1} turned stronger evidently after curing at 250°C, and at 1630 cm^{-1} there existed an absorption band of alkene

even after postcuring at 280°C. Furthermore, DSC data of PN, cured PN, and postcured PN also confirmed that large amount of alkylenic bond existed after cure, which resulted in an exothermic peak in the range of 280–400°C. So, there must exist other reactions during thermal cure that is quite different from those presented by the aforementioned researchers. Typical DSC results are listed in Table IV.

With the supporting data from FTIR and DSC, the additional reactions involved in thermal cure of PN resin may be possible, which are outlined in Scheme 3.

Thermal stability

PN resins were thermally cured at 250°C under air, as described in experimental section. Complete disappearance of $\equiv$CH absorption at 3280 cm^{-1} in FTIR spectra could ascertain the completion of cure. The thermal properties of PN resins after thermal cure were evaluated by DMA and thermogravimetric analysis (TGA) techniques. DMA profile of a typical cured PN (PN-1 in Table II) was shown in Figure 5. Obvi-

TABLE IV
DSC Characteristics of PN, Cured PN, and Postcured PN

Polymers	T_1[a] (°C)	T_2[b] (°C)	T_3[c] (°C)	ΔH (J/g)
PN[d]	198	263	296	839
	330	382	400	14.5
Cured PN[e]	238	272	298	24.4
	300	383	430	91
Postcured PN[f]	300	380	430	141
Postcured PN[g]	320	396	430	27.5

[a] Onset temperature of the exothermic peak.
[b] Peak temperature of the exothermic peak.
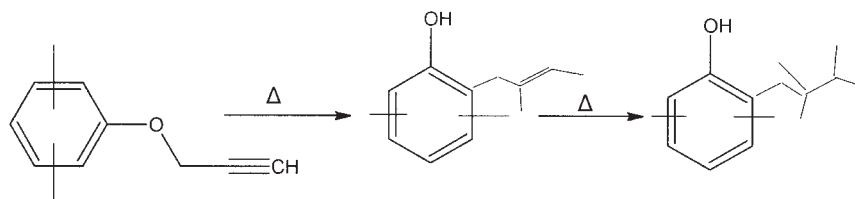[c] Endset temperature of the exothermic peak.
[d] With a propargyl content of 90% by ^{1}HNMR.
[e] Cured at 210°C for 3 h.
[f] Treated at 250°C for 2.5 h after cure.
[g] Treated at 250°C for 2.5 h then 280°C for 5 h after cure.

Scheme 3 Other possible reactions during thermal cure of PN resin.

ously, cured PN showed outstanding high thermal mechanical property, with high glass transition temperature (as high as 377°C) and low dissipation value (δ below 0.1). Here, the value of glass transition temperature of cured PN resin was remarkably higher than those reported in literature (T_g around 180–190°C).[20,21] The results implied that the PN resins can be utilized as a composite matrix for thermostructural composites.

TGA profiles in N_2 atmosphere were shown in Figure 6 for cured PN resins with varying propargyl contents, together with cured conventional novolac materials. Figure 7 showed the TGA profiles in N_2 atmosphere for cured PN resins with varying molecular weights. Etherification of phenol could improve the thermal stability of the resultant cured phenolics.[33] In the investigated coverage of propargyl contents, as propargyl content increased thermal stability (represented by the onset temperature of TGA curve) was improved a bit, and an anaerobic char residue increased slightly. This implied that thermal stability mainly depends on crosslink density and aromatic proportion. Propargyl groups could be cured into polyene, and further three-dimensional network, which is thermally resistant, and thermal stability of phenolic backbones are consolidated by crosslinked propargyl groups. Interestingly, molecular weight of PN resin hardly had any effect on thermal stability of

cured material. Maybe this is because crosslink network is mainly formed by propargyl groups and is nearly independent of the size of phenolic backbone. In all, compared with conventional cured phenolics, cured PN resin showed substantial improvement in the initial decomposition temperature (onset temperature), a decrease in the decomposition temperature (inflection temperature), and a bit more char residue. The results indicated that PN resin can be a good candidate for matrices of ablative composites. The evaluation of PN resin as matrix for composites reinforced by silica or carbon fibers will be reported later.

TGA profiles in air were shown in Figure 8 for cured PN (PN-1 in Table II), together with conventional cured novolac resin. As expected, etherification of phenol confers thermo-oxidative stability to the phenolics.[34] Cured PN resin possessed higher thermo-oxidative stability than cured novolac resin apparently. This renders PN resins better ablative property in air.

The thermal degradation behaviors of cured PN resin in N_2 and air were shown in Figure 9. Before reaching 635°C, instantaneous thermal stability in air was superior to that in N_2. In case of air, oxygen may penetrate into the cured resin, and then new structures can be formed, which are thermally more stable and can make the resultant network collapse at higher temperature.[35] Still there are small amount of unsat-
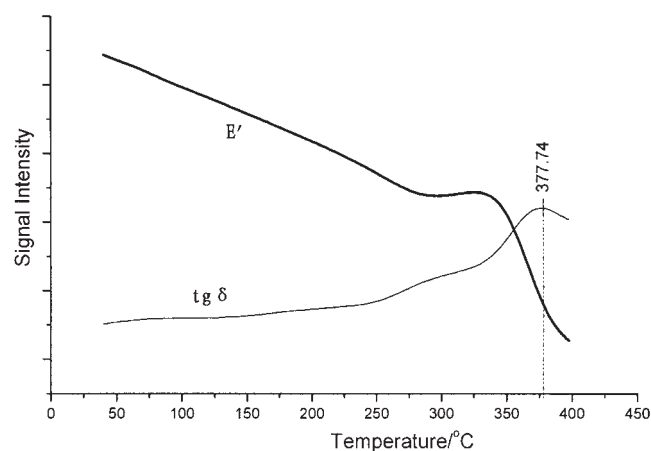

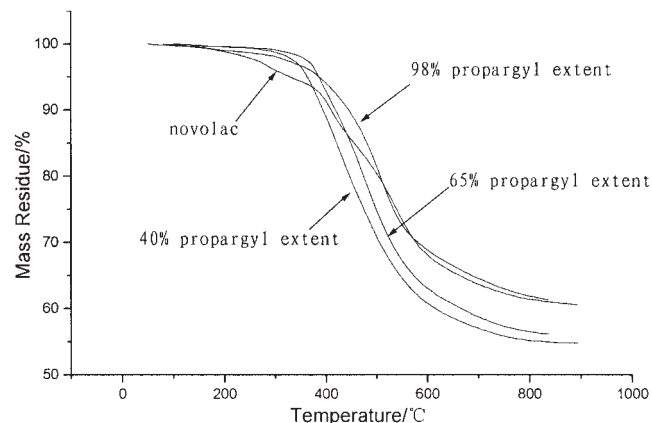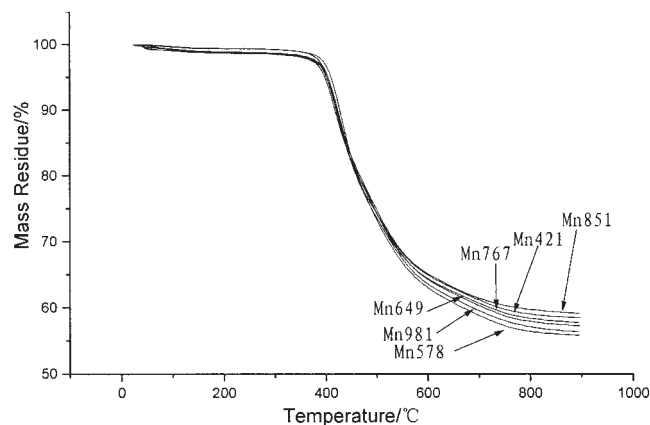**Figure 5** DMA profile of cured PN resin. (Heating rate, 5°C/min at 1 Hz.)

Figure 6 TGA profiles of cured PN resins with varying propargyl extents. (Heating rate, 10°C/min; N_2 purging rate, 30 mL/min.)
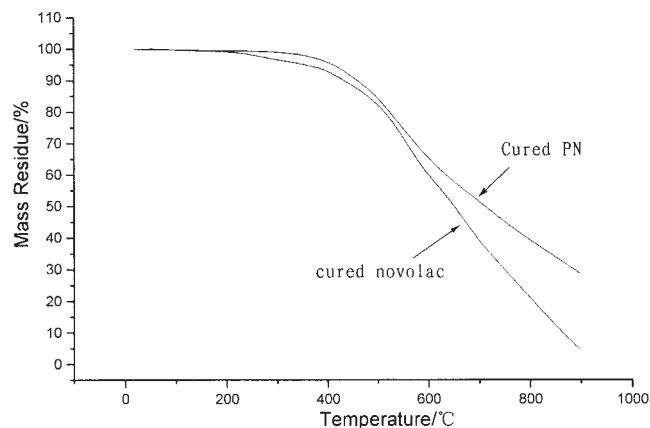
Figure 7 TGA profiles of cured PN resins with varying molecular weights. (Heating rate, 10°C/min; N₂ purging rate, 30 mL/min.)

Figure 9 TGA profiles of cured PN resins in N_2 and in air. (Heating rate, 10°C/min; gas purging rate, 30 mL/min.)
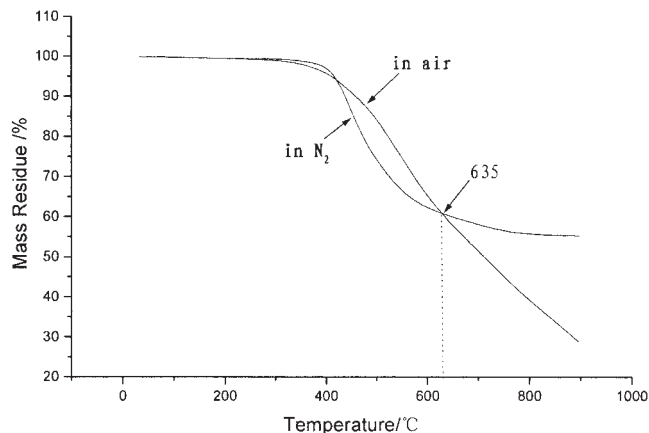
urated bonds in cured PN detected by FTIR in Figure 1, which may make the cured network easy to be oxidized.

CONCLUSIONS

Propargyl-functionalized novolac resins, with varying propargyl contents and varying molecular weights, were synthesized facilely. The structural characteristics were provided by ^{1}HNMR and FTIR techniques. Propargyl contents affect the uncatalyzed thermal cure remarkably, while molecular weights have little effect. The cure mechanism is complicated, and postcure at high temperature is required to provide entire crosslink formation and high thermal stability. DMA and TGA revealed that the cured PN resins had substantial improved thermal mechanical properties and thermal stability in comparison to the cured conventional phenolic resins. Its resistance to thermal oxidation in air is also remarkably improved. High propar-

gyl content is appreciated in view of thermal properties. We anticipate that PN resins may find considerable use in advanced thermostructural and ablative composites applications.

Figure 8 TGA profiles of cured PN and Novolac resins in air. (Heating rate, 10°C/min; N₂ purging rate, 30 mL/min.)

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