Synthesis and Thermal Properties of Ethynyl Phenyl Azo Phenol-biphenylene Resin

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ABSTRACT: A novel addition curing ethynyl phenyl azo phenol-biphenylene resin (EPABN) was synthesized by introducing ethynylphenyl group into biphenyl novolac resin (BN) through diazo coupling reaction. Its synthesis reaction and curing mechanism were also proposed. Fourier transform infrared spectroscopy and 1H NMR spectroscopic analysis showed that the ethynylphenyl group was successfully linked to the BN molecular chain. By differential scanning calorimetry analysis, the curing process of EPABN resin was determined to be 150 °C/2 h + 172 °C/2 h + 203 °C/4 h + 255 °C/4 h + 300 °C/4 h. Gel permeation chromatography and elemental analysis showed that the introduction of ethynylphenyl group increased the number-average molecular weight and weight-average molecular weight of EPABN. Thermogravimetric analysis showed that the EPABN resin synthesized under the obtained optimum conditions has excellent heat resistance, ablation resistance, and mechanical properties. Td° and Td° of heat resistance of the cured EPABN resin are 463 and 531 °C, respectively, and its residual char yield at 700 and 1000 °C is 78.2% and 72.1%, respectively.

INTRODUCTION

Phenolic resin is widely used in adhesives, laminates, ablative composites, molding compounds, coatings, foams, and many other fields due to its heat resistance, flame retardancy, low cost, and higher char yield.1–6 However, with the rapid development of high-rise buildings, aeronautics, aerospace, and other special fields, the traditional phenolic resin can no longer meet the higher requirements of these fields in terms of material strength, stiffness, heat resistance, and flame retardancy. Therefore, the research of heat-resistant, higher char yield, highly flame-retardant new phenolic resin is of great significance.7–10 The heat resistance of phenolic resin can be improved by adding modifier, which can be roughly divided into inorganic elements,11–13 inorganic nanoparticles,14,15 synthetic organic substances,16–18 natural organic substances,19,20 and composite modification.21,22 New groups such as ethynyl,23–25 allyl,26 and phthalonitrile,27,28 can also be introduced into the phenolic resin to obtain a novel addition curable phenolic resin and improve the heat resistance of the phenolic resin. Kawamoto11 prepared boron-modified phenolic resin (BPR) with salicyl alcohol and boric acid. The resin has good thermo-oxidative stability and mechanical properties. L. Asano15 obtained a phenolic resin reinforced with carbon black and mesoporous silica particles (5 and 20 wt %), which increased the glass transition temperature and mechanical properties of the silica/resin composite. Wang23 synthesized a novel phenolic resin with high ethynyl contents by the diazo coupling reaction of phenol units with 3-ethynylaniline. Most of the modification work is researched around conventional phenolic resin, but there are few studies on the modification of the high-performance phenolic resin, especially the biphenyl novolac resin (BN).29

Biphenyl novolac resin is a kind of high-performance phenolic resin that is synthesized by introducing biphenyl group into molecular main chain through Friedel–Crafts reaction between phenol and diphenyl dimethyl ether. The introduction of high rigidity biphenyl structure can greatly reduce the content of phenolic hydroxyl groups in BN resin and improve its heat resistance, low moisture absorption rate, high thermal oxygen stability, and high intrinsic flame retardancy.28,30 On the basis of this, BN was synthesized first in our work, and then ethynylphenyl group was introduced into the biphenyl novolac molecular chain to obtain a novel addition curing ethynyl phenyl azo phenol-biphenylene resin (EPABN). To the best of our knowledge, EPABN resin has been rarely reported. The structure and thermal properties of EPABN were characterized in this paper. The best curing process and the optimized synthesis reaction conditions of EPABN were discussed in detail. The synthesis of EPABN resin and its possible curing mechanism were also described. This is a new high-performance phenolic resin with high temperature resistance, higher char yield, and good process...
performance, which can be widely used in many fields such as aviation and aerospace.

**RESULTS AND DISCUSSION**

Characterization of EPABN. The FT-IR spectra of BN and EPABN samples are shown in Figure 1. It can be seen from the Fourier transform infrared (FT-IR) spectra of BN that the 3401 cm\(^{-1}\) peak is attributed to the –OH stretching vibration on the aromatic ring, the C–H stretching vibration peak at the aromatic ring is at 3022 cm\(^{-1}\), and the –CH\(_2\)– stretching vibration is at 2907 cm\(^{-1}\). 1454 and 1365 cm\(^{-1}\) correspond to the peak of C=C stretching vibration of benzene ring. 1238 cm\(^{-1}\) belongs to the peak of C–O stretching vibration on phenolic hydroxyl group. The absorption peaks at 804 and 754 cm\(^{-1}\) are the out-of-plane bending vibration absorption peaks of the para- and ortho-disubstituted phenyl C–H bond on the aromatic ring, respectively. These peaks indicate that the synthesized product is BN.

Compared with BN, the infrared absorption spectrum of EPABN is basically unchanged. Only the sharper and stronger \(\equiv\text{C}–\text{H}\) stretching vibration peak appeared at 3288 cm\(^{-1}\), and the narrow and weak \(-\text{C}–\equiv\text{C}–\) stretching vibration peak appeared at 2105 cm\(^{-1}\). The vibration peaks of 1,2,4,6-tetrasubstituted structure C–H in phenol nucleus appeared at 898 cm\(^{-1}\), and the \(\equiv\text{C}–\text{H}\) out-of-plane deformation peak of alkynyl appears near 638 cm\(^{-1}\). Strong out-of-plane bending vibration peaks of benzene ring 1,3-disubstituted C–H appeared at 798 and 691 cm\(^{-1}\). The presence of these peaks indicates that the ethynylphenyl group has been successfully linked to the BN molecular chain.

The \(^1\text{H}\) NMR spectra of the BN and EPABN samples are shown in Figure 2 (standardized against tetramethylsilane (TMS)). Figure 2a is a \(^1\text{H}\) NMR spectrum of BN, in which proton peaks from 9.6 to 9.3 ppm are attributed to internally associated phenolic hydroxyl hydrogen. Peaks from 7.6 to 7.1 ppm and from 7.1 to 6.8 ppm correspond to proton peaks of the unsubstituted hydrogen on biphenyl groups and phenol nuclear benzene rings, respectively. Peak from 4.05 to 3.75 ppm is the proton peak of methylene hydrogen. Because of the presence of isomers, the proton peak of methylene hydrogen splits into six peaks. The peak appearing around 3.4 is the proton peak of impurity water, and the peak at 2.5 is solvent dimethyl sulfoxide (DMSO) peak. Figure 2b shows the \(^1\text{H}\) NMR spectrum of EPABN. Compared with Figure 2a, the hydrogen proton peak, and the methylene hydrogen proton peak of the aryl ring were shifted to 10.9, 8.1, to 6.8, and 4.1 to 3.8 ppm, respectively. An acetylene hydrogen proton peak appeared at 4.1–4.4 ppm, confirming that ethynylphenyl group was successfully introduced into the resin’s molecular chain structure. In addition, the peaks of hydrogen proton peaks on the aromatic rings in the characteristic absorption peak of EPABN are relatively weak. This may be due to the introduction of ethynylphenyl group, making the molecular structure rigid, leading to its solubility in DMSO being not good.

The gel permeation chromatography (GPC) profiles of BN and EPABN samples are shown in Figure 3 (polystyrene (PS) standard). The profiles of the GPC curves of the BN and EPABN samples are similar, indicating that they have similar molecular weight distribution characteristics. However, the retention time corresponding to the middle peak position in the GPC curve of the EPABN sample became shorter, so that the number-average molecular weight and viscosity became large. Typical parameters of GPC curves for BN and EPABN samples are given in Table 1. We can see that the introduction of the ethynylphenyl group increases the molecular weight and viscosity of the resin.

**Table 1. Typical Parameters of GPC Curves for BN and EPABN Samples**

| resin  | \(M_\text{N}\) | \(M_\text{w}\) | polydispersity |
|--------|----------------|---------------|---------------|
| BN     | 600            | 900           | 1.50          |
| EPABN  | 1200           | 1500          | 1.25          |
of ethynylphenyl group increases the number-average molecular weight and weight-average molecular weight of EPABN, but the polydispersity becomes smaller, and the molecular weight distribution is more concentrated.

**Analysis on Curing Process of EPABN.** The EPABN resin is obtained by a coupling reaction between ethynylphenyl diazonium salt and BN, and it has an addition-curable reactive functional group in its molecular chain. This type of phenolic resin can be self-cured by thermal addition polymerization of acetylene groups at a certain temperature without the need of an external curing agent and a catalyst to obtain a cured product having excellent heat resistance. The curing process parameters can be obtained by differential scanning calorimetry (DSC) analysis.

From the DSC curve of EPABN at different heating rates given in Figure 4, the EPABN resin is a single peak cure. As the heating rate increases, its peak shape gradually broadens and high, and the peak temperature also becomes larger. When the heating rate is 5 °C/min, the peak temperature is the lowest at ~211 °C. The peak shape is the narrowest and the lowest. The reaction exothermic temperature range is 150~260 °C. The exotherm is gentle, and the curing reaction is easy to control. When the heating rate is 20 °C/min, the maximum peak temperature is ~250 °C; the exotherm of the curing reaction becomes larger, but its peak shape is the widest, indicating that the EPABN curing reaction is still easy to control.

The characteristic temperature of curing reaction of EPABN at different heating rates is shown in Table 2. As the heating rate increases, the initial curing reaction temperature ($T_i$), peak top temperature ($T_p$), and termination temperature ($T_f$) of EPABN increase. This is because, at a lower heating rate, the heat flow rate $dH/dt$ is smaller; that is, the thermal effect of unit time is small. Thus, the curing rate is small, and the system has enough time for curing reaction, so its $T_i$ is lower. As the heating rate increases, the $dH/dt$ and curing rate increase, resulting in a corresponding increase in the temperature difference, and the exothermic peak of the curing reaction will correspondingly shift toward the higher temperature. According to the DSC curve, it can be roughly determined that the curing process of the EPABN resin is 150 °C/2 h + 172 °C/2 h + 203 °C/4 h + 255 °C/4 h + 300 °C/4 h.

**Optimization of Synthesis Reaction Conditions of EPABN.** The **Mass Ratio of Different 3-Aminophenylacetylene to BN.** With ethyl alcohol absolute as the solvent, the molar ratio of 3-aminophenylacetylene to NaOH was 1:2.07. The GPC curves and N content of EPABN resins prepared from different 3-aminophenylacetylene to BN mass ratios are shown in Figure 5 and Table 3. The profile of the GPC curves of EPABN samples prepared with different 3-aminophenylacetylene and BN mass ratios are very similar, indicating that they have very similar molecular weight distribution characteristics. Table 3 shows the typical parameters of the GPC curve. As the mass ratio of 3-aminophenylacetylene to BN increases, the number-average molecular weight, weight-average molecular weight, polydispersity, and N content of EPABN increase slightly. The larger the mass ratio of 3-aminophenylacetylene to BN, the greater the amount of 3-aminobenzeneacetylene involved in the diazo reaction and the more acetylene diazonium salt positive ions available as electrophiles. The greater the chance of electrophilic substitution on the aromatic ring with biphenyl novolac, the higher the diazo coupling rate, the higher the N content in the EPABN molecule, the larger the molecular weight and the polydispersity.

**Different Molar Ratios of 3-Aminophenylacetylene to NaOH.** With ethyl alcohol absolute as solvent, the mass ratio of 3-aminophenylacetylene to BN was 1.25:1. The GPC and N contents of EPABN resins prepared from different molar ratios of 3-aminophenylacetylene to NaOH are shown in Table 4. As the molar ratio of 3-aminophenylacetylene to NaOH increases, the number-average molecular weight and weight-average molecular weight of EPABN increase, and the molecular weight distribution coefficient first decreases and then increases. But the N content in EPABN molecules gradually decreases. When the molar ratio of 3-aminophenylacetylene to NaOH is 1.25:1. The GPC and N contents of EPABN resins prepared from different molar ratios of 3-aminophenylacetylene to NaOH are shown in Table 4.

![Figure 4. DSC curves of EPABN at different heating rates (N)].(Image)

![Figure 5. GPC curves of EPABN prepared by different mass ratios of 3-aminophenylacetylene to BN (THF eluent, PS standard).](Image)

| Table 2. Characteristic Temperature of Curing Reaction of EPABN at Different Heating Rates |
|---------------------------------|------------|------------|------------|
| $\beta$, °C·min$^{-1}$ | $T_i$, °C | $T_p$, °C | $T_f$, °C |
| 5.0 | 179 | 211 | 266 |
| 10.0 | 194 | 227 | 274 |
| 15.0 | 203 | 236 | 286 |
| 20.0 | 208 | 244 | 297 |

| Table 3. EPABN Prepared from Different Mass Ratios of 3-Aminophenylacetylene to BN |
|---------------------------------|------------|------------|------------|
| mass ratio of 3-aminophenylacetylene to BN | EPABN molecular weight distribution | N content, wt % |
|---------------------------------|------------|------------|
| 1:2.5:1 | 1400 | 2600 | 1.85 | 8.49 |
| 1:4:1 | 1500 | 2800 | 1.87 | 8.51 |
| 1:5:1 | 1600 | 3000 | 1.88 | 8.55 |
Table 4. EPABN prepared from different molar ratios of 3-aminophenylacetylene to NaOH

| Molar ratio of 3-aminophenylacetylene to NaOH | EPABN molecular weight distribution (Mn, Mw, Mw/Mn) | N content, wt % |
|---------------------------------------------|-----------------------------------------------|-----------------|
| 1:1.09                                      | 1200 2000 1.25 6.00 8.97                              |
| 1:1.73                                      | 1200 1500 1.25 8.93                                   |
| 1:2.07                                      | 1400 2600 1.86 8.49                                   |
| 1:2.17                                      | 1700 4000 2.35 8.35                                   |

NaOH is 1:1.09, the N content of EPABN is the highest, but the number-average molecular weight is very low at only 200. EPABN resin has lower intrinsic viscosity and poor heat resistance. When the molar ratio of 3-aminophenylacetylene to NaOH is 1:1.73, the N content in EPABN molecule is 8.93 wt %, the lowest molecular weight distribution coefficient is only 1.25, and the molecular weight distribution is more concentrated. At this time, EPABN resin has better heat resistance. When the molar ratio of 3-aminophenylacetylene to NaOH is 1:1.73, the molecular weight of EPABN is larger, but the N content is smaller; the active acetylene group, which can be used for thermal addition curing, is less, so the heat resistance is poor. In general, the coupling rate becomes lower. The solvent water molecules can also act as catalysts to accelerate the reaction and increase the diazo coupling rate. However, when the selected solvent system is an anhydrous organic solvent, the solubility of basic aqueous solution, but the solubility of basic aqueous solution to some phenols with larger steric hindrance is poor. Therefore, the concentration of the generated phenol oxygen ions is too low, and the coupling reaction does not easily proceed. At this point, adding an alkaline substance such as ethanol or pyridine as a catalyst can accelerate the coupling reaction and increase the diazo coupling rate. However, when the selected solvent system is an anhydrous organic solvent, the solubility of NaOH and phenols deteriorates, and the diazo coupling rate becomes lower. The solvent water molecules can also act as catalysts to accelerate the reaction.

**Different Solvent Systems.** The mass ratio of 3-aminophenylacetylene to BN is 1.25:1, and the molar ratio of 3-aminophenylacetylene to NaOH is 1:1.73. The GPC and N contents of EPABN resin prepared from different solvent systems are shown in Figure 6 and Table 5. It can be seen from Figure 6 that the profiles of the GPC curves of the EPABN samples prepared with different solvent systems are very similar, indicating that they have very similar molecular weight distribution characteristics. As the water content in the solvent system increases, the number-average molecular weight, weight-average molecular weight, and polydispersity of EPABN increase first and then decrease, while the N content in the EPABN molecule continuously increases. When the solvent system used is absolute ethanol, the number-average molecular weight, weight-average molecular weight, and N content of EPABN are the smallest, but the molecular weight distribution is relatively concentrated. When the volume ratio of anhydrous ethanol to water in the solvent system is 2:1, the N content in the EPABAN is up to 9.53 wt %. The number-average molecular weight and molecular weight distribution are also relatively moderate. At this time, EPABN has excellent heat resistance. This is because the coupling reaction between diazonium salts and phenols is usually performed in weakly basic aqueous solution, but the solubility of basic aqueous solution to some phenols with larger steric hindrance is poor. Therefore, the concentration of the generated phenol oxygen ions is too low, and the coupling reaction does not easily proceed. At this point, adding an alkaline substance such as ethanol or pyridine as a catalyst can accelerate the coupling reaction and increase the diazo coupling rate. However, when the selected solvent system is an anhydrous organic solvent, the solubility of NaOH and phenols deteriorates, and the diazo coupling rate becomes lower. The solvent water molecules can also act as catalysts to accelerate the reaction.

**Thermal Properties.** EPABN Resins Prepared from Different 3-Aminophenylacetylene and NaOH Molar Ratios. The TGA curves of EPABN resin-cured products prepared from different 3-aminophenylacetylene and NaOH molar ratios are shown in Figure 7, and the typical parameters of Table 6.

Figure 6. GPC curves of EPABN prepared from different solvent systems (THF eluent, PS standard).

**Table 5. EPABN Prepared by Different Solvent Systems**

| Solvent system V(ethanol)/V(water) | EPABN molecular weight distribution (Mn, Mw, Mw/Mn) | N content, wt % |
|-----------------------------------|-----------------------------------------------|-----------------|
| Absolute ethanol                  | 1200 1500 1.25 8.93                              |
| 4:1                               | 1400 2200 1.57 9.32                              |
| 2:1                               | 1400 1900 1.36 9.53                              |

Figure 7. TG curves of the cured EPABN resin prepared from different molar ratios of 3-aminophenylacetylene to NaOH (N2, 10 °C/min).

**Table 6. Typical Parameters of the TG Curve**

| Sample | Td5%, °C | Td10%, °C | Char yield at 700 °C (%) | Char yield at 1000 °C (%) |
|--------|----------|-----------|--------------------------|---------------------------|
| 1:1.09 | 333      | 381       | 75.8                     | 59.1                      |
| 1:1.73 | 457      | 522       | 76.1                     | 70.0                      |
| 1:2.07 | 468      | 526       | 72.9                     | 64.5                      |
| 1:2.17 | 455      | 517       | 71.1                     | 62.5                      |

"Td 5%, the temperature at which 5% of the sample decomposes; Td 10%, the temperature at which 10% of the sample decomposes."
the TG curves are shown in Table 6. With the increase of the molar ratio of 3-aminophenylacetylene to NaOH, the $T_{d5}$, $T_{d10}$, char residue at 700 and 1000 °C of the cured EPABN resin first increased and then decreased. When the molar ratio of 3-aminophenylacetylene to NaOH is 1:1.09, the $T_{d5}$, $T_{d10}$, char residues at 700 and 1000 °C of the cured EPABN resin are the lowest, and the thermal performance is poor. When the molar ratio of 3-aminophenylacetylene to NaOH is 1:1.73, char residues at 700 and 1000 °C of the cured EPABN resin are the highest, which are 76.1% and 70.1%, respectively. When the molar ratio of 3-aminophenylacetylene to NaOH is 1:2.07, the cured EPABN resins $T_{d5}$ and $T_{d10}$ reach the highest, but the residual char rate is lower. Combined with GPC and elemental analysis of EPABN, it was found that EPABN resin prepared from a molar ratio of 3-aminophenylacetylene to NaOH of 1:1.73 has excellent thermal properties.

**EPABN Resin Prepared from Different Solvent Systems.**

The TG curves of the cured EPABN resin prepared from different solvent systems are shown in Figure 8, and the typical parameters of the TG curves are shown in Table 7. The $T_{d5}$, $T_{d10}$, char residues at 700 and 1000 °C of the cured EPABN resin gradually increase with the increase of the water content of the solvent system. When the solvent system used was two-thirds ethanol and one-third water (v/v), the $T_{d5}$, $T_{d10}$, char residues at 700 and 1000 °C of the cured EPABN resin reached the highest, 463 °C, 531 °C, 78.2%, and 72.1%, respectively. Combined with GPC and elemental analysis of EPABN, it can be seen that the N content of EPABN molecules synthesized under this condition is the highest, indicating that the content of active alkyne groups in the resin molecular structure is the highest. The heat-polymerization of alkyne groups increases the cross-link density of the cured EPABN resin, which greatly improves the heat resistance and ablation resistance of EPABN resins.

**Resin Synthesis Reaction and Curing Mechanism.**

The EPABN resin is obtained by using BN as raw material and introducing ethynylphenyl group into the molecular chain through a diazo coupling reaction. The reaction mechanism and curing mechanism are as follows:

1. The BN is a special phenolic resin prepared by Friedel–Crafts alkylation reaction under the action of an acidic catalyst with excess phenol and 4,4′-dichloromethylbiphenyl. The reaction mechanism is shown in Scheme 1. Under acidic condition, sodium nitrite reacts with H+ to form HNO2 and acts on 3-aminophenylacetylene to convert it into a positively charged ethynylphenyl diazo hydrochloride. Biphenyl novolac molecular chains contain a large number of phenol structures, and the ortho and para electron clouds of phenol are dense. At a pH of 8–9, ethynylphenyl diazo hydrochloride can act as an

2. EPABN is a novel addition-cure phenolic resin prepared by a diazo coupling reaction between a BN and 3-aminophenylacetylene. The reaction mechanism is shown in Scheme 2. Under acidic conditions, sodium nitrite reacts with H+ to form HNO2 and acts on 3-aminophenylacetylene to convert it into a positively charged ethynylphenyl diazo hydrochloride. Biphenyl novolac molecular chains contain a large number of phenol structures, and the ortho and para electron clouds of phenol are dense. At a pH of 8–9, ethynylphenyl diazo hydrochloride can act as an

![Figure 8. TG curves of the cured EPABN resin prepared from different solvent systems (N2, 10 °C/min).](image)

**Table 7. Typical Parameters of the TG Curve**

| sample | V(ethanol)/V(water) | $T_{d5}$, °C | $T_{d10}$, °C | char yield at 700 °C (%) | char yield at 1000 °C (%) |
|--------|---------------------|--------------|---------------|--------------------------|--------------------------|
| absolute ethanol | 457 522 | 76.1 | 70.0 |
| 4:1 | 460 527 | 77.9 | 70.4 |
| 2:1 | 463 531 | 78.2 | 72.1 |

![Scheme 1. BN Synthesis Reaction Mechanism Diagram](image)
electrophile to attack carbon atoms with a higher density of electron clouds, form intermediate products, lose hydrogen protons, and finally obtain EPABN resin. Because of the influence of steric hindrance, diazonium ions generally attack the para position, and if the para position is occupied, they will attack the ortho-position site.

(3) EPABN resin is mainly self-cured by thermal addition polymerization of ethynyl groups in the molecular chain. The ethynyl groups in the resin may be converted into benzene rings, aromatic rings, multiolefins, trimers, tetramers, conjugated olefins, etc. by trimerization reaction, Glazer coupling reaction, Strauss coupling reaction, Diels−Alder reaction, or addition polymerization reaction. The possible curing mechanism is shown in Scheme 3.

CONCLUSION

In conclusion, EPABN resin was successfully synthesized by diazo coupling reaction in this experiment. Compared with conventional high-performance phenolic resins, this is a new type of addition-curing resin in which the former needs to be cured under the action of a curing agent or a catalyst, and the latter requires only heating to be cured. The introduction of ethynylphenyl group increases the number-average and weight-average molecular weights of the resin and improves the heat resistance of the resin. The high-rigidity biphenyl structure in the molecular chain can greatly reduce the phenolic hydroxyl content in the BN resin and improve its heat resistance. Therefore, $T_d^a$ and $T_d^{10}$ of heat resistance of the EPABN resin synthesized under the optimum conditions are 463 and 531 °C, respectively, and its residual char yields at 700 and 1000 °C are 78.2% and 72.1%, respectively. The cured EPABN has excellent heat resistance, ablation resistance, and mechanical properties, which can be widely used in aerospace and aviation as ablative materials and thermal structural materials.

EXPERIMENTAL SECTION

Materials. 4,4’-Dichloromethylbiphenyl (>98%) was purchased from Jiangsu Ruifengda Chemical Materials Business
Department. Phenol and anhydrous ethanol were purchased from Sinopharm Group Chemical Reagent Co. Ltd. Methanol was purchased from Tianjin Baishi Chemical Co. Ltd. 3-Aminophenylacetylene (>98%) was purchased from Jiaozhou Fine Chemicals Co. Ltd. Sodium nitrite (NaNO₂) was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co. Ltd. Concentrated hydrochloric acid was purchased from Zhuzhou Xingkuan Chemical Glass Co. Ltd. Urea was purchased from Taishan Yueqiao Plastics Co. Ltd. Sodium hydroxide (NaOH) was purchased from Tianjin Damao Chemical Reagent Factory.

Synthesis of BN. BN resin was prepared by reacting phenol with 4,4′-dichloromethylbiphenyl in the presence of an acid catalyst. Phenol, 4,4′-dichloromethylphenyl, methanol, and concentrated hydrochloric acid were taken in a four-necked flask and stirred at 90 °C in an oil bath. The reaction was continued for 5 h under stirring at 90 °C. After the reaction is completed, it is rapidly heated to 180 °C, and the unreacted raw materials were removed by reduced pressure distillation. After it cooled, a pale yellow biphenyl novolac resin was obtained.

Synthesis of Diazonium Salts. Hydrochloric acid solution (15 wt %) was taken in a three-necked flask. 3-Aminophenylacetylene was added dropwise to it and stirred at 60 °C for half an hour. NaNO₂ aqueous solution (35 wt %) was added dropwise to the above system and stirred at −5 °C. After the addition is completed, the reaction is performed at 0 °C for 1.5 h. Finally, urea was added to neutralize unreacted nitric acid and filtered to obtain a brown-transparent diazonium salt solution.

Synthesis of EPABN. EPABN resins were prepared by coupling reaction between 3-ethylphenyl diazonium sulfate and BN in the presence of a base catalyst. Ethanol, BN, and NaOH were taken in a four-necked flask and stirred for 2 h. The solution was stirred well and cooled to 0 °C. To this solution, the synthesized diazonium salt solution was added dropwise at 0 °C and stirred well. After the addition, the solution was kept at the same temperature for 5 h by occasional stirring. The reaction mixture was then added dropwise to distilled water, and the pH was adjusted to 7 by adding dilute H₂SO₄. The synthesized resin was filtered, washed by distilled water, and dried at 60 °C overnight to obtain a reddish-brown powder EPABN resin. EPABN was thermally cured as per the following schedule: 150 °C/2 h + 172 °C/2 h + 203 °C/4 h + 255 °C/4 h + 300 °C/4 h, to give the cured thermosts.

Characterization. Spectroscopy (FT-IR) of the sample was recorded using a Nicolet 6700 Fourier transform infrared spectrometer. The data acquisition range during FT-IR analysis was from 4000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹. The sample to be tested (5 mg) was dissolved in deuterated dimethyl sulfoxide (DMSO-d₆) at a sample concentration of 10 mg/mL. The ¹H NMR spectrum of 0–15 ppm was measured at room temperature with TMS as internal standard by means of nuclear magnetic resonance spectrometer (Avance III 400 MHz). The E2695 GPC was used to measure the molecular weight size and distribution of the product. The sample was dissolved in tetrahydrofuran (THF) solvent and eluted with THF at a flow rate of 1 mL/min. The concentrations of the samples were 0.6 wt %. The standard sample was monodisperse polystyrene. The organic element analyzer (Vanio EL CHNS) was used to analyze the type and content of the elements contained in the sample. The DSC analysis (STA449C synchronous thermal analyzer) uses N₂ as the protective atmosphere; the flow rate is 60 mL/min, the heating rate is 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min, and the test temperature range is 20–350 °C. The SDTQ600 thermogravimetry differential thermal analyzer was used for thermogravimetric analysis (TGA; test temperature range of 20–1000 °C, N₂). The flow rate was 60 mL/min, and the heating rate was 10 °C/min.

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**Notes**

The authors declare no competing financial interest.

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