

Synthesis, thermal and adhesive properties of benzoxazine with acetenyl functional group

Caizhao LIU^{1,2} (刘彩召), SUN Mingming^{1,2} (孙明明), Bin ZHANG^{1,2*} (张斌), Jianhui LI¹,
Xugang ZHANG^{1,2}, Gang XUE¹, Qili LI¹, Lei WANG¹

(1. Institute of Petrochemistry, Heilongjiang Academy of Science, Harbin 150040, China; 2. Institute of Advanced Technology, Heilongjiang Academy of Science, Harbin 150020, China)

(1. 黑龙江省科学院石油化学研究院, 黑龙江 哈尔滨 150040; 2. 黑龙江省科学院高技术研究院, 黑龙江 哈尔滨 150020)

*the corresponding author, ZHANG Bin (张斌), E-mail: zhangbinaaa@sina.cn

Abstract: The novel acetylene-functional benzoxazine monomer (BB-apa) has been synthesized using 2,2-Bis(4-hydroxyphenyl)butane, 3-Aminophenylacetylene and paraformaldehyde. The structure of the monomer was well characterized by FTIR spectroscopy and ¹H NMR spectra, which indicated that the reactive oxazine ring and acetenyl group existed in molecular structure of BB-apa. The polymerization behaviour was monitored by non-isothermal differential scanning calorimetry (DSC), which shown that the introduction of ethynyl group could accelerate the ring-opening polymerization of benzoxazine monomer, leading to a lower curing temperature. Moreover, the thermoset derived from the BB-apa exhibited higher thermal stability and adhesive properties with the glass transition temperature of 353 °C compared to the traditional benzoxazine polymer without ethynyl group (BB-a).

Keywords: benzoxazine, acetenyl group, ring-opening polymerization, thermal properties, adhesive properties.

1. Introduction

High performance polymers are increasingly important in many fields, in particular aerospace, electronics and automobile industry. In recent years, polybenzoxazine has attracted great attention and emphasis as a newly advanced polymer resin due to its outstanding advantages. The attractive characteristics of benzoxazine polymers, including molecular design flexibility, low water absorption, no release of volatiles during cure and needless of harsh catalysts are of worldwide interest^[1-4]. In addition, these materials possess excellent flame-retardant^[5] and electrical properties^[6], low volumetric shrinkage upon cure^[7] and excellent chemical resistance^[8].

Generally, the thermal degradation of benzoxazine thermosets start from the thermal cleavage of Mannich base, and the pendent groups existing in the amine substituent tend to decrease the thermal stability of the polymer^[9]. There are two methods to further improve the thermal properties of benzoxazine resins. Firstly, the introduction of heterocyclic and aromatic ring structures in the polymer main and side chain structure are necessary^[10]. However, these resins tend to have high curing temperature and poor manufacturability, which limiting the scope and conditions they can be utilized; Secondly, benzoxazine monomers with varying reactive functional groups have been prepared by using different phenols or amines. The diverse functional groups such as vinyl^[11,12], allyl^[13], furan^[14], cyano^[15], norbornene^[16], imide^[17], propargyl ether^[18], acetenyl^[19], epoxy^[20] and benzoxazole^[21] can be polymerized into three-dimensional void-free networks with improved thermal properties by anchoring the dangling groups above substituents. Recently, much effort has been made to research thermally curable acetylene-containing benzoxazine with high thermal stability. Various of easily processable benzoxazine monomers with side acetylene functional groups

have been synthesized^[19]. The acetylenyl groups can react under cationic, free radical, photolytic and thermal inducement and form trimers, tetramers or conjugated polyenes^[22]. Carbon-carbon triple bonds containing benzoxazine moieties in the main chain can be prepared by Sonogashira coupling of aryl halide functional benzoxazine with Pd(PPh₃)₄ catalyst^[23]. Propargyl ether groups containing benzoxazine has been synthesized and polymerized with Rh catalyst^[24]. This polymer exhibits a high char yield of 55% by weight in nitrogen at 800 °C. Qi et al. have prepared acetylene-terminated polybenzoxazines based on Xylok prepolymer (XPBZAs)^[25]. Interestingly, the glass transition temperature of cured XPBZAs increase with the increasing content of acetylene groups due to the higher crosslink densities and lower segmental mobility.

In this paper, a well-defined alkynyl-containing benzoxazine monomer was prepared through melting method. Systematic study was carried out to study the effect of alkynyl groups of benzoxazine polymer on the curing characteristics, thermal stability, dynamic and adhesive properties compared to the alkynyl-free benzoxazine with similar structure. Results demonstrated that the acetylene-functional benzoxazine polymer presented excellent thermal and adhesive properties, and could be used for the preparation of high-performance matrix resin and high-temperature resistance adhesive.

2. Experimental

2.1. Materials

2,2-Bis(4-hydroxyphenyl)butane (bisphenol-B) (99.1%) and 3-Aminophenylacetylene (99%) were obtained from J&K Scientific Co., Ltd. Paraformaldehyde (95%), aniline (99.5%), anhydrous sodium sulfate (99%) and chloroform (99%) were purchased from Tianjin Bodi Chemicals. All solvents certified A.C.S grade and chemicals were used as received.

2.2 Synthesis

2.2.1 Synthesis of bis(3-phenylacetylene-3,4,-dihydro-2H-1,3-benzoxazinyl) isobutane (BB-apa)

A solventless synthesis procedure^[26] was used for preparation of this acetylene-functional benzoxazine monomer, bis(3-phenylacetylene-3,4,-dihydro- 2H-1,3-benzoxazinyl) isobutane (BB-apa), shown in Fig. 1(a). 2,2-Bis(4-hydroxyphenyl)butane (48.90 g, 0.1 mol), 3-Aminophenylacetylene (23.67 g, 0.2 mol), and paraformaldehyde (12.63g, 0.4mol) was added into a 250 ml three neck round-bottom flask equipped with a mechanical stirrer and refluxing condenser. After stirring at ambient temperature for 10 min, the temperature was raised to 110 °C and kept at this temperature for 0.5 h. Then, the mixture was dissolved in chloroform, and washed with 3 mol/L sodium hydroxide solution several times until the aqueous layer was colorless. The solution was washed with de-ionized water until it achieved a pH of 7, and then dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the product was dried in a vacuum oven overnight at 60 °C. The purified product was a pale yellow powder (yield: 76%) .

2.2.2 Synthesis of bis(3-phenyl-3,4,-dihydro-2H-1,3-benzoxazinyl) isobutane (BB-a)

Alkynyl-free benzoxazine monomer, bis(3-phenyl-3,4,-dihydro-2H-1,3-benzoxazinyl) isobutane (BB-a) was synthesized by following the same procedure as BB-apa, but aniline instead of 3-aminophenylacetylene. 2,2-Bis(4-hydroxyphenyl)butane, aniline and formaldehyde with a molar ratio of 1:2:4 were used for reactants, shown in Fig. 1(b). The purified product was an off-white powder (yield: 85%) .

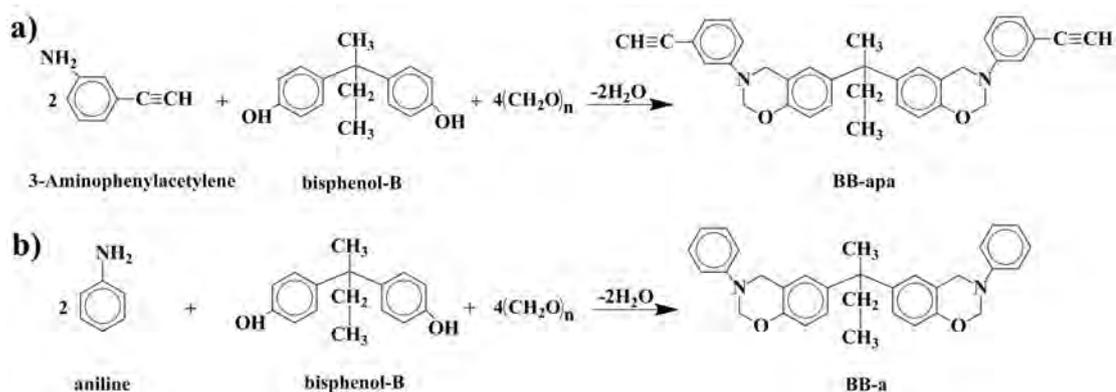


Fig. 1. Synthesis of benzoxazine BB-apa (a) and BB-a (b).

2.2.3. Preparation of benzoxazine polymer

Benzoxazine polymer, namely, poly(BB-apa) and poly(BB-a) were obtained according to the temperature programming (160 °C/2 h, 180 °C/2 h, 200 °C/2 h, 220 °C/2 h, 240 °C/2 h and 260 °C/2 h) in a vacuum drying oven, respectively. Finally, two hard dark brown solids were obtained.

2.2.4. Characterizations

The structures of the targeted monomers were verified by proton magnetic resonance spectroscopy (¹H NMR) using a Bruker AVANCE-500 nuclear magnetic resonance spectrometer at a proton frequency of 400 MHz. The solvent was deuterated chloroform and tetramethylsilane (TMS) was used as an internal standard.

The monomers were characterized by Fourier transform infrared spectroscopy (FTIR). Solid samples were prepared as KBr pellets recorded at room temperature. FTIR spectra were obtained at a resolution of 4 cm⁻¹ with co-addition of 32 scans on a Bruker-VECTOR22.

A TA Instruments DSC Model Q20 was operated with a temperature ramp rate of 10 °C/min and a nitrogen flow rate of 50 mL/min for the test of non-isothermal differential scanning calorimetric (DSC) study. Both samples were sealed in Tzero aluminum pans with lids.

Lap shear strength testing was performed according to GB/T 7124-2008 using an Instron 5969 universal testing apparatus equipped with a 30 kN load cell. Tests under 25, 200 and 350 °C were conducted at a constant crosshead-moving rate of 15 mm/min. The number of specimens tested was 5 for each temperature and an average data has been reported.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Model Q800 DMA in a single cantilever beam mode with amplitude of 30 mm and a ramp rate of 3 °C/min. The dimension of the specimens was 40 mm×2 mm×4 mm.

The thermal stability of benzoxazine polymer was investigated by the TA instruments Model Q50 thermogravimetric analyzer with a heating rate of 20 °C/min and an air flow rate of 50 ml/min or a nitrogen flow rate of 50 ml/min .

3. Results and discussion

3.1. Characterization of benzoxazine monomers

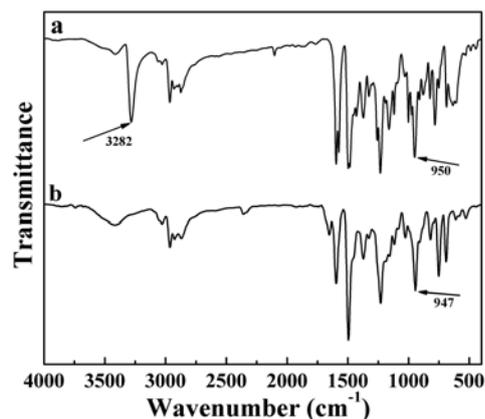


Fig. 2. FTIR spectra of BB-apa (a) and BB-a (b).

The structures of the as-synthesized benzoxazine monomers were confirmed by FTIR spectroscopy, as depicted in Fig. 2. The FTIR spectrum of BB-apa (a) showed the characteristic benzoxazine bands at 1233 and 1030 cm^{-1} which assigned to the C-O-C antisymmetric and symmetric stretching vibration, respectively. The tri-substituted benzene ring that was attached with oxazine ring appeared at 1497 and 950 cm^{-1} [16, 27-29]. The band at 3282 cm^{-1} was assigned to the the C-H stretching mode of the acetylenyl functional group, while the band at 2104 cm^{-1} was attributed to the $\text{C}\equiv\text{C}$ stretching vibration [23, 24]. The peaks of BB-a (b) at 1233 and 1030 cm^{-1} were attributed to the C-O-C antisymmetric and symmetric stretching vibration, respectively. The formation of the tri-substituted aromatic ring was confirmed by obvious characteristic peaks at around 1496 and 947 cm^{-1} .

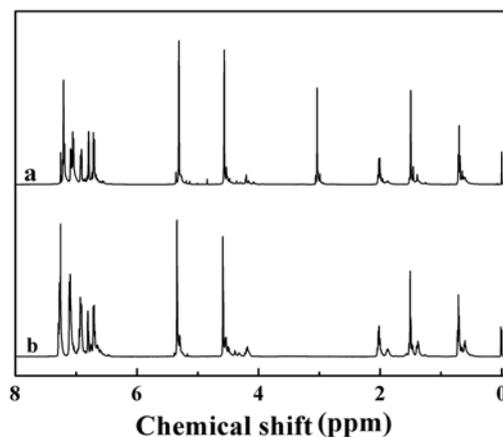


Fig. 3. ^1H NMR spectra of BB-apa (a) and BB-a (b).

The chemical structures of the novel benzoxazine monomers were also monitored by ^1H NMR spectra as shown in Fig. 3. The peak observed at 5.31 ppm for BB-apa was assigned to the $-\text{O}-\text{CH}_2-\text{N}-$ structure, while the peak at 4.56 ppm was ascribed to the $\text{Ar}-\text{CH}_2-\text{N}-$ structure of the oxazine ring, shown in Fig. 3a. The resonances at 6.70-7.25 and 2.00 ppm were separately assigned to the protons of the aromatic rings and methylene group. Besides, the resonance of the acetylenic protons was found at about 3.03 ppm [23, 24]. ^1H NMR spectrum of BB-a in Fig. 3b showed the characteristic resonances attributed to the benzoxazine structure, $-\text{O}-\text{CH}_2-\text{N}-$ and $\text{Ar}-\text{CH}_2-\text{N}-$ at 4.55, 5.30 ppm, respectively. The signals of all benzene ring were observed from 6.64 ppm to 7.29 ppm. Also, the resonances at 2.03 ppm were assigned to the protons of the methylene group. These results showed that the novel benzoxazine monomers could be synthesized by this technique.

3.2 Thermal curing behavior and adhesive properties of benzoxazine monomers

The curing process of the BB-apa and BB-a monomers were studied by non-isothermal DSC (Fig. 4) and the results were summarized in Table 1. For BB-apa, the initial reaction (T_i) and exothermic peak temperatures (T_p) were 130 and 205 °C, respectively. The DSC trace of BB-apa has only one polymerization exothermic peak, indicating the polymerization reaction of oxazine ring-opening and acetylene polymerization occur simultaneously. The values of T_i and T_p for BB-a were 194 and 235 °C, respectively. It is worth noting that the T_i and T_p of the BB-apa were shifted to lower temperatures compared to the BB-a, suggesting the incorporation of ethynyl groups can accelerate the ring-opening polymerization of benzoxazine. Moreover, the enthalpy of the BB-apa was 503 J/g, which was higher than BB-a with a value 257 J/g, this result might be explained by the introduction of reactive alkynyl groups.

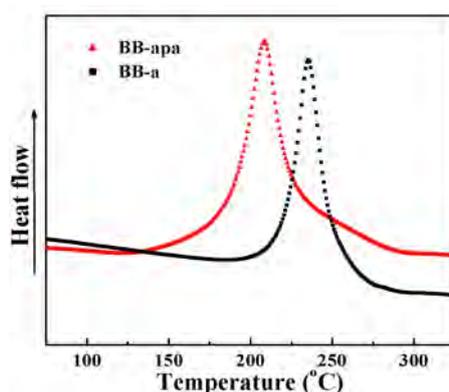


Fig. 4. DSC thermograms of BB-apa and BB-a.

Table 1. Curing characteristics and adhesive properties of BB-apa and BB-a.

Sample	T_i (°C)	T_p (°C)	ΔH (J/g)	Lap shear strength (MPa)		
				25 °C	200 °C	350 °C
BB-apa	130	208	503	10.5	12.3	3.5
BB-a	194	235	257	11.6	13.1	0.8

The adhesion on the steel plates of the alkynyl functional benzoxazine polymer, namely, poly(BB-apa) was also investigated compared with that of the conventional benzoxazine polymer poly(BB-a). The adhesive strength of the two polybenzoxazine resins were presented in Table 1. Generally, the adhesion of polybenzoxazine onto steel surfaces was acquired by the attractions between phenolic hydroxyls and iron atoms^[30, 31]. Poly(BB-apa) exhibited lap shear strength of 10.5 MPa and 12.3 MPa at 25 and 200 °C, respectively, and poly(BB-a) exhibited 11.6 MPa and 13.1 MPa, respectively. The increased bonding strength value at 200 °C may be due to softening of the cured resin. Interestingly, the lap shear strength of poly(BB-apa) was 3.5 MPa under 350 °C, while poly(BB-a) decreased to 0.8 MPa. Mainly because the poly(BB-a) had begun to decompose and lost mechanical strength in such condition, and this phenomenon could be supported by the DMA and TGA analysis results.

3.3 DMA and TGA analysis

Fig. 5 displayed the temperature dependence of the storage modulus (E'), loss modulus (E''), and loss factor ($\tan\delta$) for polymerized BB-apa and BB-a. The results were summarized in Table 2. In general, the storage modulus of the solid material under shear deformation provided information relating to the material stiffness. The E' of poly(BB-a) with a value 3.9 GPa at 25 °C decreased rapidly at about 170 °C shown in Fig. 5a, while that of poly(BB-apa) was almost unchanged with values 3.8-2.1 GPa for a wide temperature range up to 320 °C, which could be attributed to their enhanced

network structure formation. The glass-transition temperature (T_g) was separately determined from the peak maximum of E'' and $\tan\delta$ curve, which was corresponded to the transition from the glassy state to the rubbery state. For example, the T_g of the poly(BB-a) shown in Fig. 5b and 5c was 177 and 196 °C from the E'' and the $\tan\delta$ curve, respectively. On the other hand, the T_g of poly(BB-apa) were centered at 336 and 353 °C, respectively. As expected, the introduction of alkynyl groups led to a significant increase in T_g by about 160 °C, since the rigid backbone of high crosslink-density had been formed and then restricted the movement of the polymer chains. It was noteworthy that the E'' and $\tan\delta$ curves of poly(BB-apa) showed an additional broad transition from 220 °C to 310 °C mainly corresponding to further polymerization reactions of the unreacted acetylene groups or its secondary reactions^[32]. DMA results revealed that the presence of alkynyl groups can significantly improve the T_g and the dynamic thermal mechanical properties of polybenzoxazine.

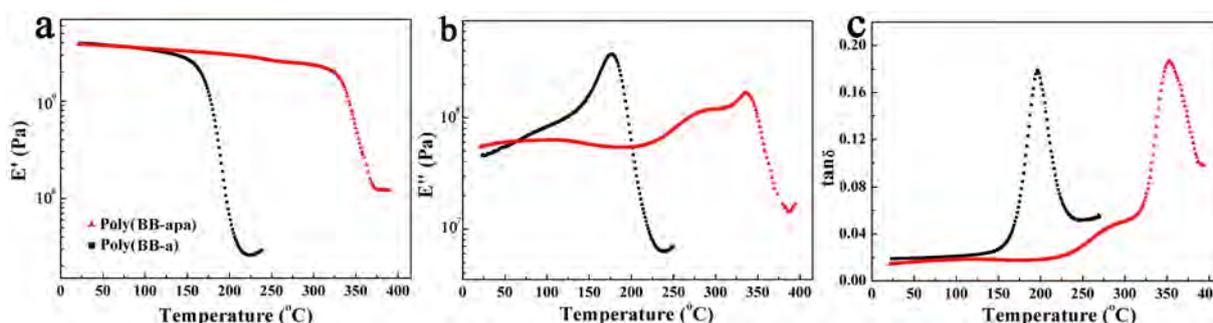


Fig. 5. Storage modulus (a), loss modulus (b), and loss factor (c) for poly(BB-apa) and poly(BB-a).

The thermal stability of the cured benzoxazines under air and nitrogen atmosphere were investigated by TGA. Generally, the relative thermal stability of these samples was estimated by comparing values of 5 and 10% weight loss temperatures (T_5 and T_{10}) and also the char yield under different temperature and atmosphere. As shown in Fig. 6 and Table 2, the T_5 and T_{10} of the poly(BB-apa) were at 392 and 402 °C in air (Fig. 5a), and increased up to 400 and 409 °C in nitrogen (Fig. 5b), respectively. The T_5 and T_{10} of poly(BB-a) without acetylenyl groups were at 316 and 355 °C in the air, and 315 and 335 °C in nitrogen, respectively. It was clearly observed that the weight loss temperature was considerably increased by the introduction of acetylenyl groups in the monomer. Furthermore, the char yield of the poly(BB-apa) were 47% at 500 °C under air and 50% at 800 °C under nitrogen, respectively, which were much higher than those of poly(BB-a) (ca. 45% at 500 °C under air and 29% at 800 °C under nitrogen). The TG results demonstrated that the reactive acetylenyl groups act as additional cross-linking points could effectively inhibit aniline component degradation, which resulted in the enhancement of the thermal properties.

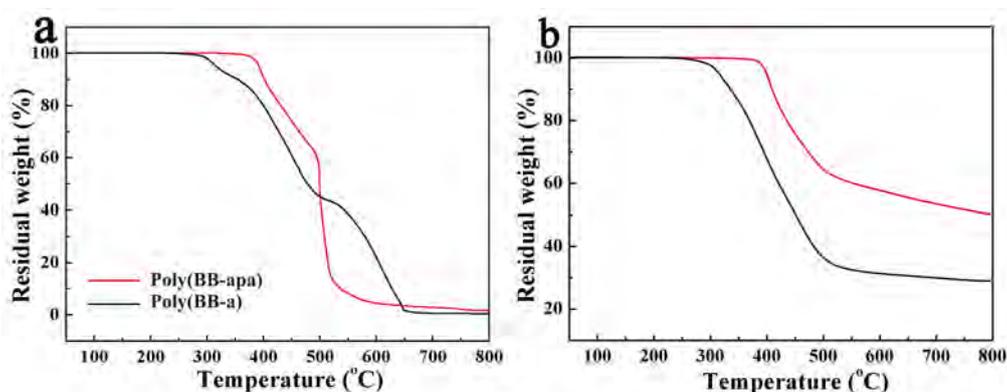


Fig. 6. TGA thermograms of poly(BB-apa) and poly(BB-a) in air (a) and nitrogen (b).

Table 2. DMA and TG analysis results of poly(BB-apa) and poly(BB-a).

Sample	DMA results				TG results					
					Air			Nitrogen		
	E',25 °C (GPa)	E',200 °C (GPa)	TgE'' (°C)	Tgtanδ (°C)	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char yield (%) ^c	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char yield (%) ^d
PBB-apa	3.8	3.0	177	196	392	402	47	400	409	50
PBB-a	3.9	0.7	336	353	316	355	45	315	335	29

^a The 5% weight loss temperature in air and nitrogen atmosphere, respectively.

^b The 10% weight loss temperature in air and nitrogen atmosphere, respectively.

^c Char yield at 500 °C in air atmosphere.

^d Char yield at 800 °C in nitrogen atmosphere.

4. Conclusions

An acetylenyl functional benzoxazine (BB-apa) and a non-acetylenyl based benzoxazine (BB-a) were synthesized, and characterized by FTIR and ¹H NMR spectra, respectively. The acetylenyl groups in benzoxazine monomer had served as a cure accelerator, which resulted in the lower initial polymerization temperature and peak temperature. The polybenzoxazine derived from BB-apa exhibited higher thermal stability, T_g, and thermo mechanical properties than analogous polybenzoxazine due to the higher cross-linking density. The cured resin char yield achieved 47% at 500 °C under nitrogen and 50% at 800 °C under air. The average lap shear strength of BB-apa polymer was up to 3.5 MPa under 350 °C. This acetylene-functional benzoxazine monomer showed potential for high temperature adhesive applications and could be used as a matrix of high performance composites.

Acknowledgements

This work was supported by the youth innovation Foundation of Heilongjiang Academy of Sciences, China (Grant No. 2015-Y-06).

References

- [1]Ishida H, Rodriguez Y. Curing kinetics of a new benzoxazine-based phenolic resin by differential scanning calorimetry[J]. Polymer, 1995, 36(16): 3151-3158.
- [2]Ishida H, Low H Y. A study on the volumetric expansion of benzoxazine-based phenolic resin[J]. Macromolecules, 1997, 30(4): 1099-1106.
- [3]Chernykh A, Liu J, Ishida H. Synthesis and properties of a new crosslinkable polymer containing benzoxazine moiety in the main chain[J]. Polymer, 2006, 47(22): 7664-7669.
- [4]Chernykh A, Agag T, Ishida H. Novel benzoxazine monomer containing diacetylene linkage: An approach to benzoxazine thermosets with low polymerization temperature without added initiators or catalysts[J]. Polymer, 2009, 50(14): 3153-3157.
- [5]Espinosa M A, Galia M, Cadiz V. Novel phosphorilated flame retardant thermosets: epoxy-benzoxazine-novolac systems[J]. Polymer, 2004, 45(18): 6103-6109.
- [6]Yeganeh H, Razavi-Nouri M, Ghaffari M. Investigation of thermal, mechanical, and electrical properties of novel polyurethanes/high molecular weight polybenzoxazine blends[J]. Polymers for Advanced Technologies, 2008, 19(8): 1024-1032.
- [7]Liu X, Gu Y. Study on the volumetric expansion of benzoxazine curing with different catalysts[J]. Journal of applied polymer science, 2002, 84(6): 1107-1113.
- [8]Kim H D, Ishida H. Study on the chemical stability of benzoxazine-based phenolic resins in carboxylic acids[J].

Journal of applied polymer science, 2001, 79(7): 1207-1219.

[9]Low H Y, Ishida H. An investigation of the thermal and thermo-oxidative degradation of polybenzoxazines with a reactive functional group[J]. Journal of Polymer Science Part B Polymer Physics, 1999, 37(7): 647-659.

[10]Wu Y C, Kuo S W. Synthesis and characterization of polyhedral oligomeric silsesquioxane (POSS) with multifunctional benzoxazine groups through click chemistry[J]. Polymer, 2010, 51(17): 3948-3955.

[11]Liu Y X, Ma H M, Liu Y, et al. A well-defined poly (vinyl benzoxazine) obtained by selective free radical polymerization of vinyl group in bifunctional benzoxazine monomer[J]. Polymer, 2016, 82: 32-39.

[12]Takeichi T, Thongpradith S, Kawauchi T. Copolymers of Vinyl-Containing Benzoxazine with Vinyl Monomers as Precursors for High Performance Thermosets[J]. Molecules, 2015, 20(4): 6488-6503.

[13]Dumas L, Bonnaud L, Olivier M, et al. Bio-based high performance thermosets: Stabilization and reinforcement of eugenol-based benzoxazine networks with BMI and CNT[J]. European Polymer Journal, 2015, 67: 494-502.

[14]Dumas L, Bonnaud L, Olivier M, et al. High performance bio-based benzoxazine networks from resorcinol and hydroquinone[J]. European Polymer Journal, 2016, 75: 486-494.

[15]Cao G P, Chen W J, Liu X B. Synthesis and thermal properties of the thermosetting resin based on cyano functionalized benzoxazine[J]. Polymer degradation and Stability, 2008, 93(3): 739-744.

[16]Zhang K, Ishida H. Thermally stable polybenzoxazines via ortho-norbornene functional benzoxazine monomers: Unique advantages in monomer synthesis, processing and polymer properties[J]. Polymer, 2015, 66: 240-248.

[17]Zhang K, Liu J, Ohashi S, et al. Synthesis of high thermal stability polybenzoxazoles via ortho-imide-functional benzoxazine monomers[J]. Journal of Polymer Science Part A: Polymer Chemistry, 2015, 53(11): 1330-1338.

[18]Agag T, Takeichi T. Novel benzoxazine monomers containing p-phenyl propargyl ether: polymerization of monomers and properties of polybenzoxazines[J]. Macromolecules, 2001, 34(21): 7257-7263.

[19]Kim H J, Brunovska Z, Ishida H. Synthesis and thermal characterization of polybenzoxazines based on acetylene-functional monomers[J]. Polymer, 1999, 40(23): 6565-6573.

[20]Rao B S, Palanisamy A. Synthesis of bio based low temperature curable liquid epoxy, benzoxazine monomer system from cardanol: Thermal and viscoelastic properties[J]. European Polymer Journal, 2013, 49(8): 2365-2376.

[21]Zhang K, Zhuang Q, Liu X, et al. A new benzoxazine containing benzoxazole-functionalized polyhedral oligomeric silsesquioxane and the corresponding polybenzoxazine nanocomposites[J]. Macromolecules, 2013, 46(7): 2696-2704.

[22]Ratto J J, Dynes P J, Hamermesh C L. The synthesis and thermal polymerization of 4, 4'-diethynylphenyl ether[J]. Journal of Polymer Science: Polymer Chemistry Edition, 1980, 18(3): 1035-1046.

[23]Dogan Demir K, Kiskan B, Yagci Y. Thermally curable acetylene-containing main-chain benzoxazine polymers via sonogashira coupling reaction[J]. Macromolecules, 2011, 44(7): 1801-1807.

[24]Kiskan B, Yagci Y. Synthesis and characterization of thermally curable polyacetylenes by polymerization of propargyl benzoxazine using rhodium catalyst[J]. Polymer, 2008, 49(10): 2455-2460.

[25]Qi H, Pan G, Zhuang Y, et al. Synthesis and characterization of acetylene-terminated polybenzoxazines based on polyaralkyl-phenolic prepolymer[J]. Polymer Engineering & Science, 2010, 50(9): 1751-1757.

[26]Ishida H. Process for preparation of benzoxazine compounds in solventless systems: U.S. Patent 5,543,516[P]. 1996-8-6.

(more references goto p151)