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A Novel Polybenzoxazine Containing Styrylpyridine Structure via the Knoevenagel Reaction

Huachuan Zhang, Min Li, Yuyuan Deng, Chengxi Zhang, Qichao Ran, Yi Gu
State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, People's Republic of China
Correspondence to: Y. Gu (E-mail: guyi@scu.edu.cn) and Q. Ran (E-mail: qichaoran@126.com)

ABSTRACT: In this article, a kind of styrylpyridine-containing polybenzoxazine was obtained via the Knoevenagel reaction between benzaldehyde and methylpyridine groups. The benzoxazine monomer (MPBC) containing the benzaldehyde and methylpyridine groups was synthesized firstly and its structure was characterized by Fourier transform infrared (FTIR) spectra, ^{1}H NMR and ^{13}C NMR. With the aid of differential scanning calorimetry, FTIR, and photoluminescent tests, the interesting curing behaviors were probed. The results showed that the ring-opening polymerization occurred at lower temperature, and the Knoevenagel reaction further took place at elevated temperature. The amine and phenol moieties were bonded together to form the styrylpyridine structure. Due to these special crosslinking structures, the corresponding polybenzoxazine exhibited excellent thermal stability, and had a special high char yield of 74.5%. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40823.

KEYWORDS: crosslinking; ring-opening polymerization; thermal properties

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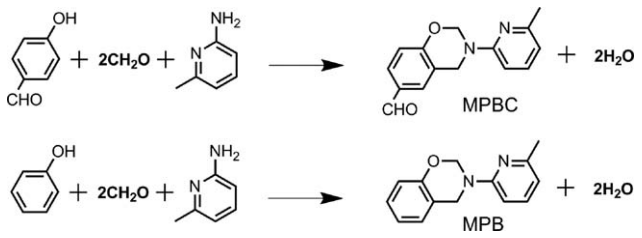
INTRODUCTION

Polybenzoxazines are a kind of polymer with —CH_2—NR—CH_2— structure via the thermally activated ring opening polymerization of corresponding benzoxazine monomers synthesized from formaldehyde, phenol or phenol derivatives, and primary amines. Due to the attractive properties, such as good processability, near-zero shrinkage and no byproducts released during the ring-opening polymerization, superior mechanical property, high thermal stability, and low water absorption, they have been used in many fields such as microelectronics and aeronautical technology.[1–4] Due to their distinctive advantages of polybenzoxazines over other equally excellent thermally resistant polymers, further studies on improved thermal resistance is desired.

As reported in previous studies, the cleavage of Mannich Bridge can form volatile fragments in polybenzoxazines at high temperature.[5–8] As in the case of mono-benzoxazine, such as phenol–aniline based benzoxazine, the breaking of C—N bond will form primary aniline, phenolic fragments, which may volatilize during the pyrolysis process. If the phenol or aniline is anchored to the crosslink network, the fragments will have a longer residence time in the bulk before evaporation, as a result the thermal resistance of polybenzoxazines can be improved. Thus, one method to improve the thermal property is the synthesis of benzoxazines based on bisphenol containing thermal stable structure such as furan,[9] carbonyl,[10] sulfone,[11] phenolphthalein,[12] fluorine,[13,14] and triazine groups[15] etc., because the release of phenolic species is retarded. Introducing additional reactive function groups such as benzocyclobutene,[16] nitrile,[17–20] maleimide,[21,22] and propargyl ether[23] groups etc., to the aniline moiety of benzoxazines is another effective method to enhance the thermal stability. However, to a certain extent, the existence of monoamine or monophenol in above benzoxazines still affects the improvement of the thermal stability.

Additionally, the main-chain type polybenzoxazines also show good thermal stability because the moieties of both amine and phenol are bonded together through chemical bonds. It can be supported by the fact that the first weight loss peak almost completely disappear for the main-chain type polybenzoxazines in derivative thermogravimetric analysis (TGA) thermograms.[24–27] During their thermal decomposition, the fragments are not easily evaporated and have longer retention time in bulk phase, although the Mannich Bridge is broken. However, the viscosity of those main-chain benzoxazines is relatively high and the processing ability is unsatisfactory.

In this study, therefore, we attempt to synthesize a novel benzoxazine monomer containing aromatic aldehyde and methylated derivatives of pyridine, which can undergo the Knoevenagel reaction to form the styrylpyridine structure.[28,29] As reported, the pyridyl-functional benzoxazine has a higher char yield than aniline based benzoxazine.[30] Our research showed that the phenol



Scheme 1. Synthesis of MPBC and MPB.

and amine moieties were bonded together by —C═C— bond after the ring-opening polymerization and the Knoevenagel condensation reaction. The corresponding styrylpyridine-containing polybenzoxazine exhibited excellent thermal stability.

EXPERIMENTAL

Materials

Phenol (98%), 2-amino-6-methylpyridine (98%), 2-aminopyridine (98%), and *p*-hydroxybenzaldehyde (98%) were purchased from Aladdin Industrial Corp. (China). Paraformaldehyde (96 %) was supplied by Fydsa (Spain). Sodium hydroxide (NaOH) and toluene were purchased from Chengdu Kelong Chemical Reagents Corp. (China). All chemicals were used as received.

Synthesis of Monomers

As shown in Scheme 1, 3-(6-methylpyridin-2-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carbaldehyde (MPBC) was synthesized from paraformaldehyde, 2-amino-6-methylpyridine, and *p*-hydroxybenzaldehyde. To a three-necked 250 mL round-bottomed flask was added paraformaldehyde (0.41 mol) and 2-amino-6-methylpyridine (0.2 mol) dissolved in toluene (80 mL). After stirring for 30 min at 30°C, *p*-hydroxybenzaldehyde (0.2 mol) was added, and then the reaction was refluxed for 5 h at 80°C. After the mixture was cooled to room temperature it was washed with 1 mol/L aqueous sodium hydroxide and water for three times to remove the impurities. After that, the solvent was removed by a rotary evaporator. A light red viscous product was obtained (yield = 87.9%). ^{1}H NMR (DMSO-d_6, ppm): 9.83 (s, —CHO), 7.78–6.63 (m, Ar—H), 5.78 (s, O—CH_2—N), 4.99 (s, Ar—CH_2—N), 2.33 (s, —CH_3). ^{13}C NMR (DMSO-d_6, ppm): 191.28 (—CHO), 159.53–105.35 (Ar—C), 75.76 (O—CH_2—N), 44.72 (Ar—CH_2—N), 24.11 (—CH_3). Fourier transform infrared (FTIR) (KBr, cm^{-1}): 941 (oxazine ring), 1024 (symmetric stretching of C—O—C), 1166 (asymmetric stretching of C—N—C) 1234 (asymmetric stretching of C—O—C), 1384 (symmetric stretching of —CH_3), 1498 (stretching of trisubstituted benzene ring), 1687 (stretching of —C═O).

3-(6-Methylpyridin-2-yl)−3,4-dihydro-2H-benzo[e][1,3]oxazine (MPB) as a reference compound was synthesized from paraformaldehyde, 2-amino-pyridine, and *p*-hydroxybenzaldehyde using the same method. A light yellow liquid product was obtained (yield = 92.1%). ^{1}H NMR (DMSO-d_6, ppm): 7.52–6.63 (Ar—H), 5.63 (s, O—CH_2—N), 4.87 (s, Ar—CH_2—N), 2.33 (s, —CH_3). ^{13}C NMR (DMSO-d_6, ppm): 157.76–104.95 (Ar—C), 74.78 (O—CH_2—N), 44.82 (Ar—CH_2—N), 24.15 (—CH_3). FTIR (KBr, cm^{-1}): 942 (oxazine ring), 1034 (symmetric stretching of C—O—C), 1145 (asymmetric stretching of C—N—C), 1222 (asymmetric stretching of C—O—C), 1379 (symmetric stretching of —CH_3), 1488 (stretching of disubstituted benzene ring).

Characterization

^{1}H NMR and ^{13}C NMR measurements were carried out using a Bruker TD-65536 NMR (400 MHz), with DMSO-d6 (dimethyl sulfoxide) as the solvent and tetramethylsilane as the internal standard. FTIR spectra were collected in KBr pellets using a Nicolet Magna 650 spectrophotometer at a resolution of 4 cm^{-1}. The scanned wavenumbers range from 4000 to 400 cm^{-1}. Differential scanning calorimetry (DSC) thermograms were obtained from a TA instrument model Q20 at a heating rate of 10°C/min with a nitrogen flow rate of 60 mL/min. Photoluminescent (PL) emission spectra were recorded on a Hitachi model F-7000 fluorescence spectrophotometer. Molecular simulation was conducted with the software Material Studio 4.0 (Accelrys). Density functional theory method with local density approximation calculation was performed using the Dmol3 program. TGA were performed on a TA Instruments High Resolution Q600 thermogravimetric analyzer under nitrogen atmosphere at a flow rate of 60 mL/min with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Synthesis of Benzoxazine Monomers

In this study, a novel benzoxazine containing benzaldehyde and methylpyridine groups was synthesized successfully. It should be noted that this synthesis reaction of MPBC is special, because the aldehyde group on phenol can easily react with the primary amine to form the Schiff base structure. If the primary amine was consumed firstly by the aldehyde group, the oxazine ring will not be generated because of the lack of the amine. So, to avoid this side reaction, 2-amino-6-methylpyridine reacted first with paraformaldehyde by adjusting the adding order. After the amino groups reacted, the *p*-hydroxybenzaldehyde was added to further form the oxazine ring.

The chemical structures of the monomers MPB and MPBC were confirmed by FTIR spectra (Figure 1), ^{1}H NMR, and ^{13}C NMR (Figure 2). For MPBC, the absorption appeared at 941 cm^{-1} proved the formation of the oxazine ring. The absorption at 1687 cm^{-1} was corresponded to the characteristic stretching of —C═O. The ^{1}H NMR was used to further confirm the structure of MPBC. The resonances of the oxazine ring were observed at 4.99 and 5.78 ppm which were assigned to Ar—CH_2—N and O—CH_2—N, respectively. The chemical shift

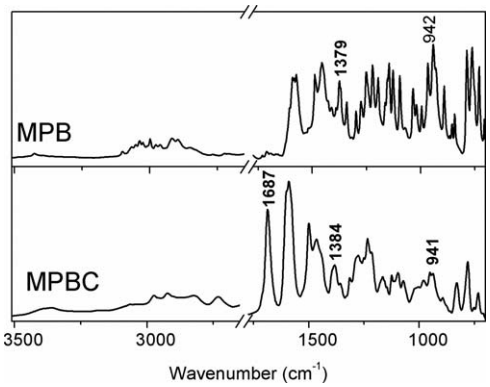


Figure 1. FTIR spectra of MPB and MPBC.

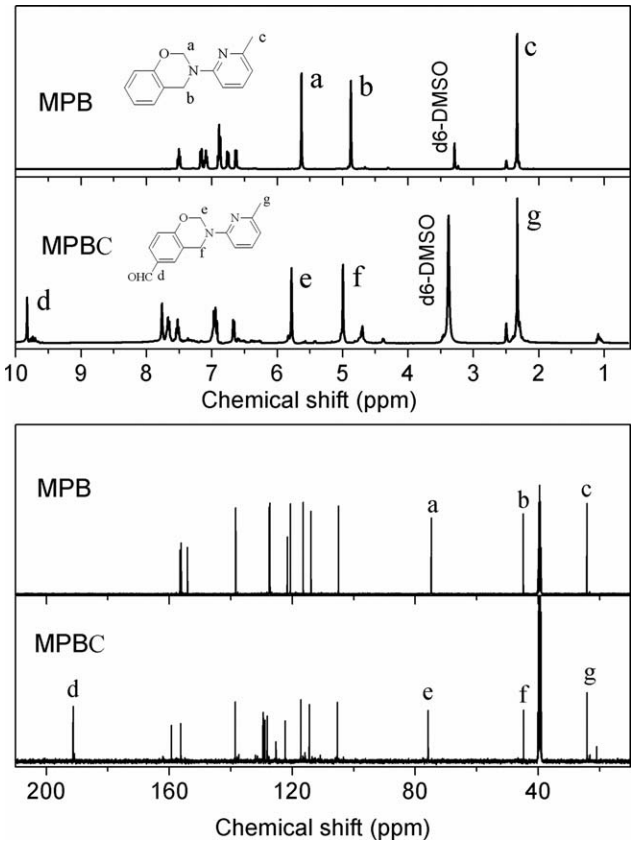


Figure 2. ^{1}H NMR and ^{13}C NMR spectra of MPB and MPBC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 9.83 ppm was assigned to the proton of the aldehyde group. As detailed in ^{13}C NMR spectra, the chemical shifts at 44.72, 75.76, and 191.28 ppm were assigned to Ar—CH_2—N, O—CH_2—N, and —C═O, respectively. For MPB, the absorption appeared at 942 cm^{-1} was due to the oxazine ring. The resonances of the oxazine ring were observed at 4.87 and 5.63 ppm. The characteristic results showed that the benzoxazine monomers were successfully synthesized.

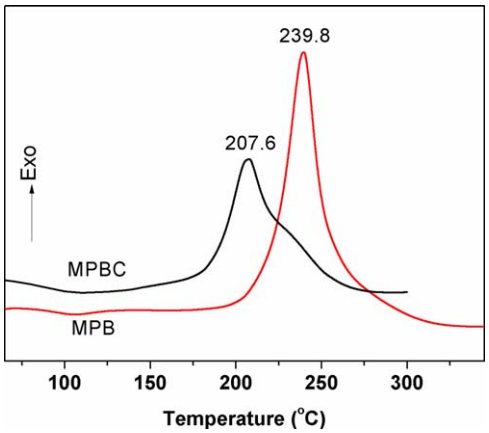


Figure 3. DSC thermograms of MPB and MPBC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

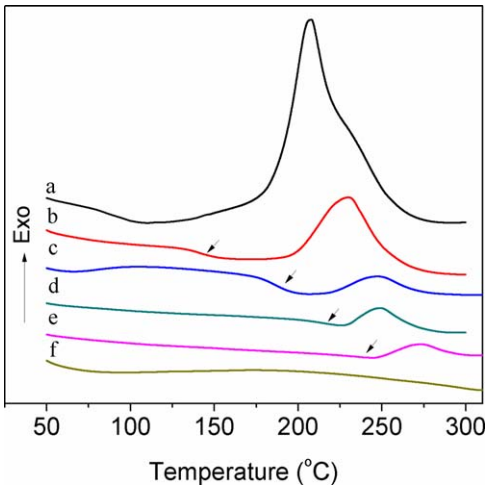


Figure 4. DSC thermograms of MPBC (**a**) and its polymers cured at 160°C/5 h (**b**), 180°C/5 h (**c**), 200°C/2 h (**d**), 220°C/2 h (**e**), and 250°C/2 h (**f**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Curing Behaviors of Benzoxazine Monomers

The curing behaviors of MPBC and MPB were studied by DSC. As shown in Figure 3, the exothermic peak temperature of MPB without the aldehyde group was at 239.8°C, which is lower than that of aniline based benzoxazine; that is probably caused by the pyridyl group.[30] The exothermic curve of MPBC with the aldehyde group turned wide with a range from 150°C to 280°C and the peak was at 207.6°C. Obviously, the thermally activated ring-opening polymerization temperature of MPBC is much lower than that of MPB. It should be attributed to the fact that the electron-withdrawing character of the aldehyde group in MPBC can promote the thermally activated ring-opening reaction of benzoxazine.[10] Additionally, the DSC curve of MPBC showed an obvious shoulder peak around 230°C. This means that the curing process of MPBC probably contains other cross-link reactions besides the polymerization of the oxazine ring and the reaction may involve aldehyde groups.

To further understand the curing behavior of MPBC, the polybenzoxazines cured at different temperatures were studied as detailed in Figure 4. The primary values are summarized in Table I. After cured at 160°C, the exothermic peak at 207.6°C originated from the ring-opening polymerization shifted to a high temperature and the enthalpy was 92.3 J/g. A low glass transition temperature (T_g) was observed at 141.1°C (line b) meaning that the polymer network was formed incompletely. After cured at 180°C, the onset temperature of the exothermic peak was around 216.3°C and only 20.7 J/g enthalpy was left. The T_g rapidly increased to 186.7°C (line c). This result indicated that the cross-linking structure formed by the ring-opening polymerization was further improved. The ring-opening polymerization of benzoxazines is generally finished after curing 200°C.[12,31] However, for poly(MPBC) cured at 200°C/2 h (line d), a small exothermic peak still existed with an enthalpy of 19.0 J/g, which only decreased 1.7 J/g compared with the sample cured at 180°C. This small change demonstrated that just a few reactions took place at 200°C. This small exothermic peak may be the "shoulder

Table I. DSC Parameters of Poly(MPBC) Cured at Different Temperatures

Sample	T_{onset} (°C)	T_{peak} (°C)	T_g (°C)	ΔH (J/g)
a	150	207.5	-	356.9
b	193.9	230.3	141.1	92.3
c	216.3	247.7	186.7	20.7
d	229.2	250.1	215.7	19.0
e	248.1	271.9	232.1	11.9
f	-	-	-	0

peak" mentioned above, suggesting that additional crosslinking reactions existed at an elevated temperature. For poly(MPBC) cured at 220°C/2 h (line e), the enthalpy decreased to 11.9 J/g and the T_g further increased to 232°C, meaning that additional crosslinking reaction took place after the ring-opening polymerization. After curing at 250°C/2 h (line f), no exothermic peak was observed, revealing that the second polymerization finished. The T_g was too high to examine for this sample. This additional reaction is probably the Knoevenagel reaction. A nucleophilic addition of an active hydrogen compound (—CH_3) to a carbonyl group (—CHO) followed by a dehydration reaction, as we expect.

Polymerization Reaction of MPBC

The change of the chemical structures of MPBC at different curing temperatures was studied by the FTIR spectra. As shown in Figure 5, after curing at 160°C for 5 h (b), 180°C for 5 h (c), the characteristic absorption of the oxazine ring at 941 cm^{-1} almost disappeared. At the same time, the intensity of the typical absorption attributed to the aldehyde group at 1687 cm^{-1} and the characteristic absorption of methyl at 1384 cm^{-1} did not change. That meant the ring-opening polymerization of the oxazine ring took place firstly and the Knoevenagel reaction of the methyl and aldehyde group may not begin at 180°C. When the curing temperature was increased to 200°C and above, the typical band of the aldehyde at 1687 cm^{-1} and the methyl at 1384 cm^{-1} disappeared simultaneously, which indicated the aldehyde and methyl groups has begun to reacted. In the meanwhile, a new sharpen peak appeared at 1632 cm^{-1} representing the stretching of —C═C— as the curing temperature increased, which gives a clear evidence about the occurrence of the Knoevenagel reaction (Scheme 2).

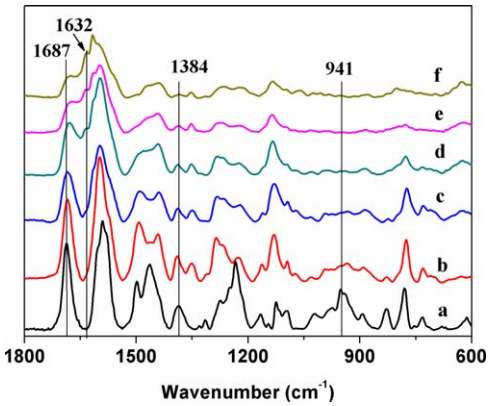
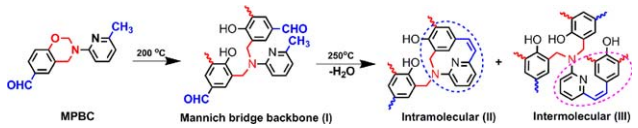


Figure 5. FTIR spectra of MPBC (**a**) and its polymers cured at 160°C/5 h (**b**), 180°C/5 h (**c**), 200°C/2 h (**d**), 220°C/2 h (**e**), and 250°C/2 h (**f**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Furthermore, the relative concentration variation of the methyl and aldehyde groups was calculated from the peak height. The peak of benzene band absorbance at 1596 cm^{-1} was chosen as an internal reference because the half width at half height of this peak of the samples was 43 ± 1 cm^{-1} nearly the same. A multi-peaks Gaussian fitting was applied to deal with the overlapped curves. The relative concentration was calculated by $H_R(T)/H_{1596}(T)$, where $H_R(T)$ is the peak height of R (methyl or aldehyde) absorbance band after cured at temperature (T), $H_{1596}(T)$ is the peak height of 1596 cm^{-1}. The relationship of the concentration versus the temperature obtained from the FTIR results is shown in Figure 6. As can be seen, the relative concentration of those groups only showed a slightly change after cured at 180°C, suggesting that nearly no reaction occurred. Obviously, after cured at 200°C, a sudden change of the concentrations of the methyl and aldehyde groups was observed simultaneously. As the curing temperature rise, the concentrations of the methyl and aldehyde groups decreased at the same time. This result also proves the occurrence of the Knoevenagel reaction from the methyl and aldehyde groups.

As a result, the phenol and amine moieties are bonded together via —C═C— bond. The styrylpyridine structure is formed in the network of poly(MPBC), as illustrated in Scheme 2. The styrylpyridine structure is a repeat unit of polystyrylpyridine (PSP) resins which exhibit excellent heat resistance, mechanical property and flame retardancy.[32–34] Therefore, the thermal properties of poly(MPBC) must be improved dramatically. It also should be pointed out that the styrylpyridine structure might be formed through the intramolecular or intermolecular Knoevenagel condensation reactions, as shown in Scheme 2,



Scheme 2. Ring-opening polymerization and Knoevenagel reaction of MPBC upon curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

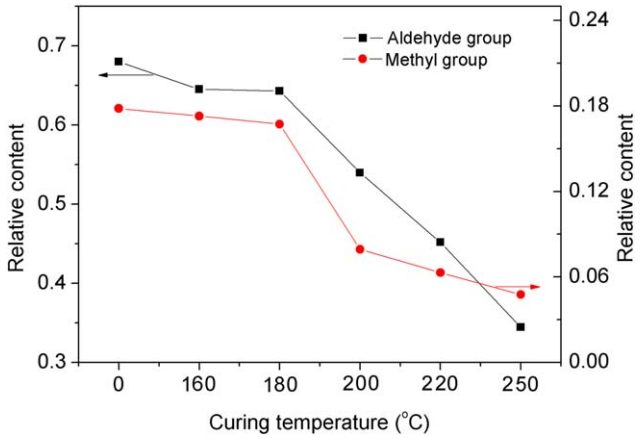


Figure 6. The relationship of concentration versus temperature obtained from FTIR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structures II and III, and both structures can increase the crosslinking density of polybenzoxazine.

To further prove the existence of the Knoevenagel reaction, the weight loss from the Knoevenagel condensation reaction can be tracked by comparing the TGA curves of poly(MPBC) cured at different temperatures. As detailed in TGA, derivative thermogravimetry (DTG) and DSC curves are shown in Figure 7. Poly(MPBC) cured at 200°C showed an obvious weight loss stage from 230°C to 280°C (line d and d′) and an exothermic peak appeared at the same range (line d″). This result indicated that some crosslinking reactions with the weight loss taken place at this temperature range. The reaction should be the Knoevenagel reaction. Because the ring-opening polymerization of the oxazine ring has no byproduct released and should occur before 200°C.[12,31] The weight loss should come from the condensation reaction of the aldehyde and methyl groups in MPBC. Moreover, the initial and maximum weight loss temperatures and the exothermic peak of poly(MPBC) cured at 220°C (line e, e′, and e″) turned to the high temperatures, and the weight loss curve also matched well with the heat flow plot. This result suggested that the additional crosslinking reaction took place under heat-treatment at 220°C. The crosslinking density further increased so that the Knoevenagel reaction of the aldehyde and methyl groups became more difficult. Thus, the high reaction temperature was needed. Almost no degradation was observed before 300°C for poly(MPBC) cured at 250°C and no exothermic peak was seen, which revealed the Knoevenagel reaction had nearly finished after 250°C.

Another evidence to support the formation of styrylpyridine structure is the PL feature of poly(MPBC). PL spectra of polymer powder under excitation at 489 nm were illustrated in Figure 8. Poly(MPBC) cured at 160°C (line b) and 200°C (line d), with backbone primarily consisting of Mannich bridge (Scheme 2, structure I), displayed a PL emission at about 489 nm from polybenzoxazine. After cured at 250°C, as detailed in Scheme 2, structures II and III, poly(MPBC) displayed an additional PL emission at about 567 nm, which should be contributed to the styrylpyridine structure generated from the Knoevenagel reaction.[35,36]

Usually, the Knoevenagel condensation reaction of the methyl and aldehyde groups takes place from 150°C to 200°C.[28,37] But the Knoevenagel reaction in this work occurred at a high temperature range. It is known that the addition reaction of a nucleophilic methylene onto a carbonyl group is the first step in the Knoevenagel reaction.[34] The charge densities of the methyl and aldehyde carbon atoms probably determine the difficulty of this reaction. As shown in Table II, the charge densities of the carbon atoms in each compound were calculated by density functional theory method with local density approximation calculation, which was performed using the Dmol3 program embedded in Material Studio 4.0 package. The charge densities of the carbon atoms in 2-methylpyridine, 2-amino-6-methylpyridine, and MPBC are almost equivalent. The charge densities of the carbon atoms on *p*-hydroxybenzaldehyde and MPBC are lower than that of benzaldehyde, which suggests the reactivity of the carbonyl on MPBC is lower than benzaldehyde.

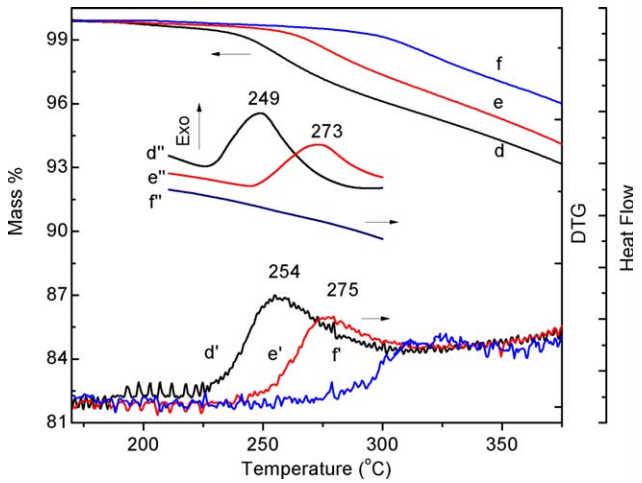


Figure 7. TGA, DTG, and DSC thermograms of poly(MPBC) cured at 200°C (d, d′, d″), 220°C (e, e′, e″), and 250°C (f, f′, f″). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

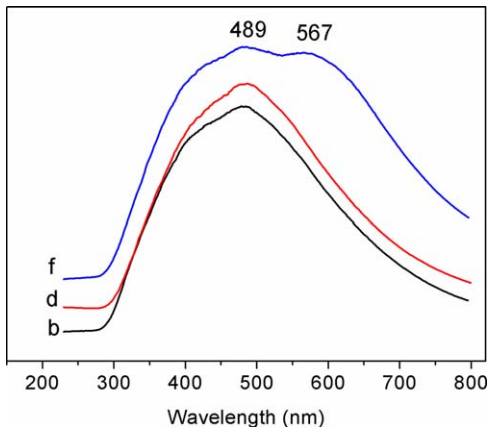
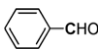
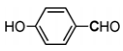
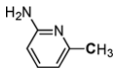
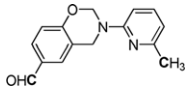
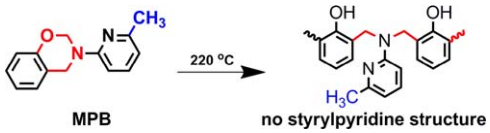


Figure 8. PL spectra of poly(MPBC) cured at 160°C (b), 200°C (d) and 250°C (f) under excitation at 489 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Charge Density of C Atom of Methyl or Aldehyde Group

Compound						
Charge density of C atom	—**C**HO/0.123	—**C**HO/0.115	—**C**H_3/−0.072	—**C**H_3/−0.072	—**C**HO/0.114	—**C**H_3/−0.071



Scheme 3. Polymer structure of poly(MPB). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This is why the reaction temperature of the Knoevenagel reaction increased during the cure of MPBC.

Thermal Stability of Cured Resins

To better understand the styrylpyridine structure in poly(MPBC), a reference compound MPB was used. Undoubtedly, the Knoevenagel reaction cannot take place and no styrylpyridine can be formed during the polymerization of MPB, as illustrated in Scheme 3, because there is no aldehyde group in this monomer. Figure 9 illustrates the thermal stability of poly(MPBC) and poly(MPB). The temperatures at 5% and 10% weight loss of poly(MPBC) were 398°C and 475°C, respectively. The temperatures at 5% and 10% weight loss of poly(MPB) were 306°C and 350°C, respectively. The char yield of poly(MPBC) was 74.5% that is much higher than that of poly(MPB), which had a char yield of 48.1%. In the case of polybenzoxazines containing functional groups, such as furan, carbonyl, sulfone, phenolphthalein, benzocyclobutene, nitrile, and maleimide, their char yields were lower than 65%.[9–20] However, the char yield of poly(MPBC) exceeded this value, suggesting the approach in this work can enhance the thermal stability dramatically. This was attributed to the special chemical structures formed via Knoevenagel reaction.

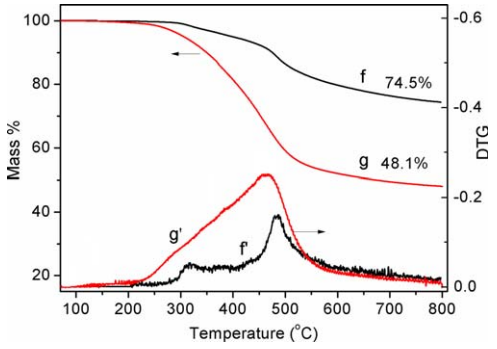


Figure 9. TGA and DTG thermograms of poly(MPBC) (f, f′ cured at 250°C) and poly(MPB) (g, g′ cured at 220°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It has been reported that the derivative curves of a TGA thermogram contain a lot of information on revealing the crosslinking structures of polybenzoxazines.[38,39] For classical bisphenol and aniline-based polybenzoxazines,[38,40] the initial weight loss stage is assigned to the weight loss of free primary aniline, and then the release of phenolic species, the pyrolysis of the char is the last weight loss event. The derivative curves of poly(MPB) and poly(MPBC) are shown in Figure 9. The weight loss rate of poly(MPBC) was smaller than that of poly(MPB) through the pyrolysis process. That meant less primary amine and phenolic species were released during the degradation of poly(MPBC). Because the Knoevenagel crosslinking reaction hanged the amines and phenol moieties into the polymeric network by the thermostable —C═C— bond.

CONCLUSIONS

A novel styrylpyridine-containing polymer was designed and prepared from benzoxazine monomer with benzaldehyde and methylpyridine groups. The Knoevenagel reaction was studied by DSC, FTIR, and PL tests. The styrylpyridine structure, which bonded the amine and phenol moieties together, was generated after the ring-opening polymerization and the Knoevenagel reaction. Due to the special styrylpyridine structure, the corresponding polybenzoxazine exhibited excellent thermal stability, which is expected to be applicable in spaceflight as a high-performance material.

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