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A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4′-diaminodiphenyl sulfone-based benzoxazine monomer

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ABSTRACT

The first successfully synthesized benzoxazine in high purity from 4,4′-diaminodiphenyl sulfone (DDS), paraformaldehyde and phenol using high boiling point nonpolar solvent is reported. The solution method for benzoxazine synthesis is modified by using a nonpolar solvent of high boiling point. For comparison, the synthesis of such difficult benzoxazine monomer was prepared in high boiling point polar solvent, dimethylsufoxide. ^{1}H NMR indicates the purity of the monomer prepared by this novel method to be quite high in comparison with that obtained using dimethylsulfoxide (DMSO). The thermally activated polymerization of the monomer affords polybenzoxazine with T_g at ca. 203 °C. The 5% and 10% decomposition temperatures of the polymer are 324 and 368 °C with 58% char yield, reflecting the excellent thermal stability than the typical polybenzoxazine based on bisphenol-A and aniline.

1. Introduction

Over the last decade, an interesting addition-cure phenolic resin, namely benzoxazine, has attracted much attention of the research community because of its unique advantages over most of the known polymers. The chemistry of benzoxazine is responsible for a number of inherent processing advantages, including low melt viscosity, no harsh catalyst required, no volatile release during cure and minimal cure shrinkage [1–3]. Polybenzoxazines also exhibit good dielectric properties and low water absorption at saturation (<2%), and thus are excellent candidates for electronic packaging applications. They also have a good thermal stability that is demonstrated by their high glass transition temperatures, degradation temperatures, and char yields [4–7]. A unique combination of intramolecular and intermolecular hydrogen bonding also contributes to the properties of polybenzoxazines [8–12].

The vast majority of polybenzoxazine studies are based on benzoxazine monomers derived from the reaction of bisphenols and monofunctional amines [13–16]. A wide variety of available bisphenols offers great opportunities in molecular design to tailor polybenzoxazines for specialty applications. A few number of benzoxazine monomers derived from diamines and monofunctional phenols is reported. Allen and Ishida have recently developed [17,18] a series of aliphatic diamine-based benzoxazine monomers. These monomers were easily synthesized using a monofunctional phenol with linear aliphatic diamines by varying the length of the linear aliphatic chain. The diamine-based benzoxazine with a short aliphatic chain demonstrated the ability to polymerize at lower temperatures to give the polymer with a comparable glass transition temperature (T_g) and improved mechanical properties to the traditional polybenzoxazines. Agag et al. prepared novel benzoxazine based on poly(oxypropylene)diamine oligomers, showing advantageous properties including the low melt viscosity of benzoxazine precursors and high flexibility of their thermosets [19,20]. Although the synthesis of aliphatic diamine-based benzoxazine was successful, the synthesis of aromatic diamines-based benzoxazine was seldom studied. Men and Lu have recently prepared a series of diamine-based benzoxazine precursors using 4,4′-diaminodiphenyl methane (DDM) and different phenolic derivatives including phenol, *p*-cresol, and 2-naphthol. However, the purity of phenol/DDM-based benzoxazine was very poor (<50%) [21].

The synthesis of aromatic diamine-based benzoxazines is generally hampered by the poor solubility of many aromatic diamines in the preferred solvents used for benzoxazine preparation. Also, the formation of stable triaza network structure resulted from the condensation of diamine and formaldehyde suppresses the reaction to continue for benzoxazine formation. In addition, the other side condensation reactions are quite possible. All these factors led to a difficulty for aromatic diamine-based benzoxazine preparation. The success to synthesize aromatic diamine-based benzoxazines with the large varieties of the commercially available aromatic diamines can undoubtedly increase the scope of molecular design flexibility of benzoxazines and hence expand their applications.

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In the current study, we report new methodology for the preparation of high-purity aromatic diamine-based benzoxazines in solution. The new method adopted is especially useful in achieving high yield synthesis using aromatic, weak amines, such as 4,4′-diaminodiphenyl sulfone for which no successful high yield and purity synthesis has been reported. The preparation of the monomer and the properties of its polymer will be discussed.

2. Experimental

2.1. Materials

Phenol (99%), and 4,4′-diaminodiphenyl sulfone (DDS) (99%) were used as received from Aldrich. Paraformaldehyde and methylenedianiline (MDA) (>98%) were used as received from Merck. All solvents were used as received from Aldrich.

2.2. Preparation of 3,3′-(4,4′-sulfonylbis(4,1-phenylene))bis-(3,4-dihydro-2H-benzo[e][1,3]oxazine) [P-DDS]

2.2.1. Method 1

In a 100 mL flask were dissolved DDS (100 mmol, 24.83 g) and phenol (200 mmol, 18.82 g) in 50 mL DMSO. Paraformaldehyde (600 mmol, 18 g) was added to the solution followed by heating the mixture at 150 °C in a preheated oil bath. By following the reaction by ^{1}H NMR, it was found that the best conversion to cyclic benzoxazine structure was achieved after ca. 60 min. The solution was cooled and poured into 1 L of 1 N aqueous sodium hydroxide solution. The precipitate was collected by filtration, and washed with water several times. The precipitate was finally washed several times with methanol, followed by drying at 50 °C under vacuum to afford pale yellow powder (35 g, 72%).

2.2.2. Method 2

A mixture of DDS (100 mmol, 24.83 g), phenol (200 mmol, 18.82 g) and paraformaldehyde (600 mmol, 18 g) was poured in 200 mL mixed isomer xylenes. The milky mixture was heated gradually and was kept stirring at 150 °C. The formation of triaza gel was observed after ca. 10 min. The formation of benzoxazine monomer through triaza structure as intermediates has been reported. The insoluble gel has been observed and characterized in other reports [22,23]. After ca. 3 h, the insoluble white color gel coagulated into yellow highly viscous product at the bottom of the flask due to the limited solubility in xylenes. The reaction mixture was stirred for additional 3 h at the same condition. The reaction mixture was cooled to room temperature and then poured into hexane to eliminate xylenes. The rest of the solid product in the flask was washed several times with hexane. The product was dissolved in dimethylformamide (DMF), precipitated in 1 N aqueous solution of sodium hydroxide to remove any phenolic compounds, washed several times with water and finally with methanol. The product was dried under vacuum at 50 °C for 24 h to afford pale yellow powder (39 g, 81%).

2.3. Measurements

^{1}H and ^{13}C NMR spectra were acquired in deuterated dimethylsufoxide on a Varian Oxford AS600 at a proton frequency of 600 MHz and its corresponding carbon frequency. The average number of transients for ^{1}H and ^{13}C is 64 and 1024, respectively. A relaxation time of 10 s was used for the integrated intensity determination of ^{1}H NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Coaddition of 32 scans was recorded at a resolution of 4 cm^{-1}. Transmission spectra were obtained by casting a thin film on a KBr plate for partially cured samples. A differential scanning calorimetry (DSC) was performed on TA Instruments DSC model 2920 with a heating rate of 10 °C/min and a nitrogen flow rate of 60 mL/min for all tests. All samples were crimped in hermetic aluminum pans with lids. Dynamic mechanical analyses were done on a TA Instruments Q800 DMA applying controlled strain tension mode with amplitude of 10 μm and a temperature ramp rate of 3 °C/min. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA with a heating rate of 10 °C/min in a nitrogen atmosphere.

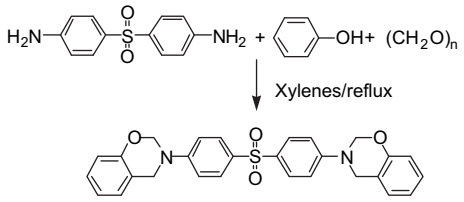
3. Results and discussion

3.1. Preparation of DDS-based benzoxazine monomer

Benzoxazine monomers can be generally synthesized either in solution or melt process. While both methods work well for synthesis of many benzoxazines, they have some limitations for preparing certain benzoxazines. The patented melt state process [24] usually affords monomers with high purity and a high yield. However, this method is not successful when aromatic diamines are used, due to the formation of hard mass of triaza structure as mentioned previously, which is difficult to mix. In solution process, a nonpolar solvent is found to be a favorable choice for benzoxazine formation because the polar solvents allow side reactions and initiate the ring opening of benzoxazine structure, leading to poor yield of benzoxazine monomer [25]. The most common solvents for the synthesis of benzoxazine monomers are chloroform, dioxane, and toluene. The disadvantage of this method is that a long synthesis time is needed for the preparation of the monomer; sometimes days are needed to decompose the intermediate of insoluble triaza structure, especially when aromatic diamines are used. Also, the poor solubility of many aromatic amines makes it difficult to synthesize benzoxazines from many interesting diamines. Thus, there is a need to develop a complementary new method to overcome the shortcomings associated with the use of the aforementioned conventional methods.

The current method is based on the use of nonpolar solvent with high boiling point. The high boiling point solvent as a reaction medium allows to carry out the reaction at high temperature (>150 °C), which offers increased solubility for the reaction components. It was also found that the rate of decomposition of the triaza structure was higher at an elevated temperature. Thus, benzoxazine formation with difficult amines in such solvent at high temperature becomes possible.

Although a few aromatic diamine-based benzoxazines have been reported [21], the formation of DDS-based benzoxazine is particularly hindered in comparison with other amines. This is quite obvious because of the reduced basicity of the primary amine group in DDS which is attributed to the electron-withdrawing resonance effect of the sulfonyl group [26]. In this study, the novel method for benzoxazine formation in which a nonpolar solvent at high temperature has been applied to prepare phenol/DDS benzoxazine type (P-dds). P-dds was prepared in a high boiling polar solvent for comparison. Scheme 1 shows the preparation of P-dds. When the reaction was performed at higher temperature in DMSO as a polar solvent, the system was homogenous and the decomposition of triaza gel was fast. By following the reaction by ^{1}H NMR, it was observed that the longer the reaction time, the greater the side reactions. We have found that the oxazine ring formation is more efficient when the dielectric constant of the reaction medium is smaller [25,27]. The dielectric constant of DMSO is 47, whereas those of xylene isomers are; *o*-xylene, $\varepsilon = 2.6$; *m*-xylene, $\varepsilon = 2.4$; and *p*-xylene, $\varepsilon = 2.3$. These dielectric constants are comparable to



Scheme 1.

traditionally favored solvents, such as chloroform ($\varepsilon = 3.7$), 1,4-dioxane ($\varepsilon = 2.2$) and toluene ($\varepsilon = 2.4$); however, the high boiling point of xylenes (bp = 140 °C) is advantageous as described earlier in comparison to chloroform (bp = 61.2 °C), 1,4-dioxane (bp = 101.0 °C), and toluene (bp = 110.6 °C). Further advantage of high boiling solvent is that the dielectric constant of a material tends to lower as the use temperature increases. The best conversion to cyclic benzoxazine structure was achieved after ca. 50–60 min. However, when xylenes were used as solvent at ca. 150 °C, the reaction rate was slower and the complete decomposition of triaza gel took longer time (~3 h). The slow reaction rate is due to the heterogeneous nature of the reaction since DDS was insoluble in xylenes and the product was partially soluble in xylenes as well. To our surprise, the formation of oligomers as a result of the polymerization of formed benzoxazine was minimal even at this high temperature.

The structure of the monomer was confirmed by ^{1}H NMR and FTIR. Fig. 1 shows the ^{1}H NMR spectra of P-dds prepared by the two methods. The characteristic resonances of oxazine ring assigned with the –CH_2–N– and –O–CH_2–N– protons appeared as two singlets at 4.55 and 5.42 ppm, respectively. The multiplet at 6.72–7.82 ppm is assigned to the aromatic protons. The Mannich bridge protons of opened oxazine rings are typically located at approximately ~4 ppm and thus the presence of any proton peaks in this region indicates the formation of ring opened oligomeric species from the monomers. Thus, the resonance at 4.2 ppm for monomer obtained by the DMSO method indicates low purity of the monomer. On the other hand, the integration analysis of the proton peaks shows that the closed ring content of benzoxazine monomer obtained from the xylene method to be better than 98% which is unusually high compared to the traditional benzoxazine synthesis conditions. The solubility of the starting material in DMSO and the instability of the triaza gel at higher temperature allowed the reaction to proceed quickly in DMSO. However, the solubility of P-dds in DMSO increased the possibility of ring opening of benzoxazine structure at higher temperature. When xylenes were used

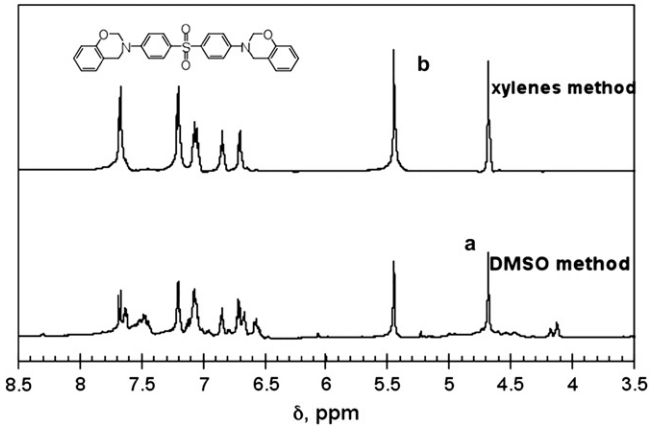


Fig. 1. ^{1}H NMR spectra of DDS-based benzoxazine monomer.

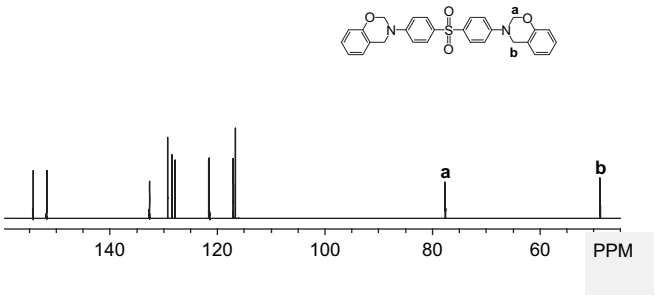


Fig. 2. ^{13}C NMR spectra of DDS-based benzoxazine monomer.

as a solvent, although DDS was insoluble, the reaction proceeded successfully in this heterogeneous system in mere 3 h while maintaining the cyclic benzoxazine structure at this high temperature. It is noteworthy mentioning that when dioxane was used as a solvent at ca. 100 °C, more than a week was needed to decompose the triaza gel structure.

Fig. 2 is the corresponding ^{13}C NMR spectrum also supporting the notion of high-purity compound. The two singlets at 77.50 ppm and 58.75 ppm are typical of the carbon resonances of –N–CH_2–O– and –N–CH_2–Ph of the oxazine ring, respectively. No detectable resonances due to impurities are seen in the spectrum.

The structure of P-dds was further confirmed by FTIR. There are a number of infrared bands in the spectra, highlighted in Fig. 3, which can be used to confirm the formation of oxazine ring structure.

The presence of cyclic ether of benzoxazine structure is confirmed by the absorbance peaks at 1035 and 1228 cm^{-1} due to the C–O–C symmetric stretching and asymmetric stretching modes, respectively. The characteristic mode of benzene with an attached oxazine ring is located at 955 cm^{-1}. The absorption bands characteristic of *ortho*-disubstituted benzene appeared at 1601 cm^{-1} and as well as 755 cm^{-1}. The infrared spectrum for the polymerized monomer was also recorded after several polymerization cycles. The absorbance bands associated with the closed oxazine ring have completely been consumed during the ring opening polymerization. These include the absorption contributed from the stretching modes of the cyclic aromatic ether at 1035 and 1228 cm^{-1}, as well as the characteristic band of the benzoxazine structure at 955 cm^{-1}.

The thermally activated polymerization behavior of P-dds was studied by DSC. The non-isothermal polymerization thermogram is

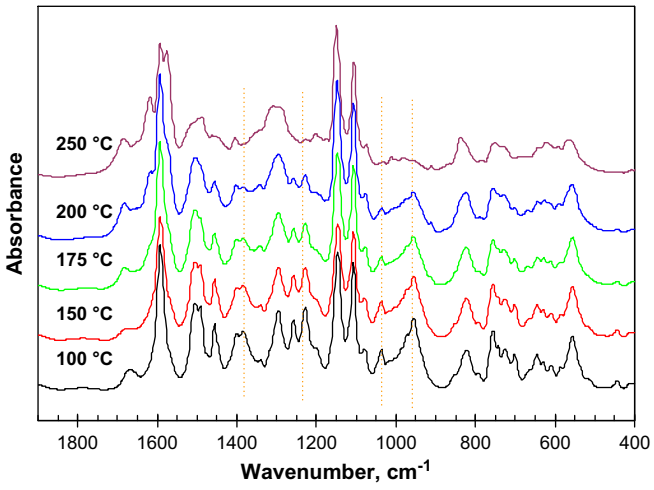


Fig. 3. IR spectra of P-dds monomer after thermal treatment.

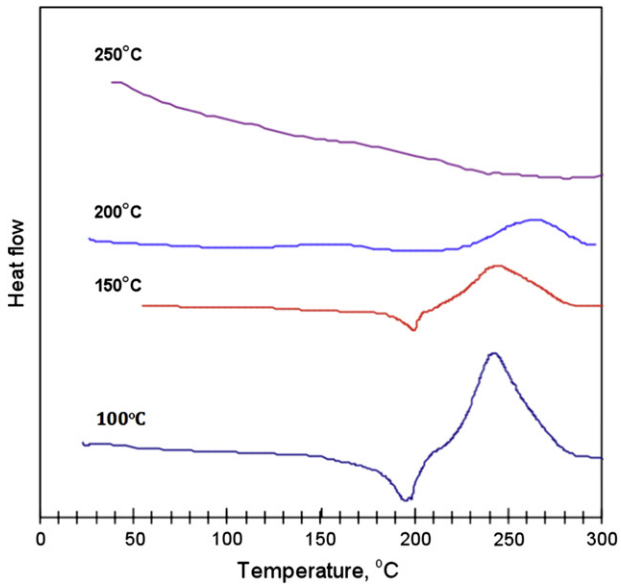


Fig. 4. DSC thermograms of P-dds monomer after thermal treatment at various temperatures.

shown in Fig. 3. An exothermic peak was observed due to the ring opening polymerization. The onset of the exotherm starts at 218 °C and reaches the maximum at 239 °C. The DSC traces after each polymerization cycle was also evaluated as shown in Fig. 4. It can be seen that the exothermic peak gradually decreases after each polymerization cycle and disappears by the end of the heating at 250 °C/30 min. The DSC and IR results indicate that the polymerization of the monomer effectively completed by the end of the 250 °C heating cycle.

The thermal properties of poly(P-dds) after gradual heating up to 250 °C were studied and compared with a standard polybenzoxazine (poly(BA-a)) which is based on bisphenol-A and aniline. The viscoelastic analysis of the P-dds monomer after gradual heating up to 250 °C was examined.

Fig. 5 shows the temperature dependence of the storage modulus, loss modulus and tan δ for the polybenzoxazines. The storage modulus (E') of 3.7 GPa at room temperature suggests higher stiffness of the polymer. The glass transition temperature as defined by the peak position of E'' is around 190 °C. However, due to

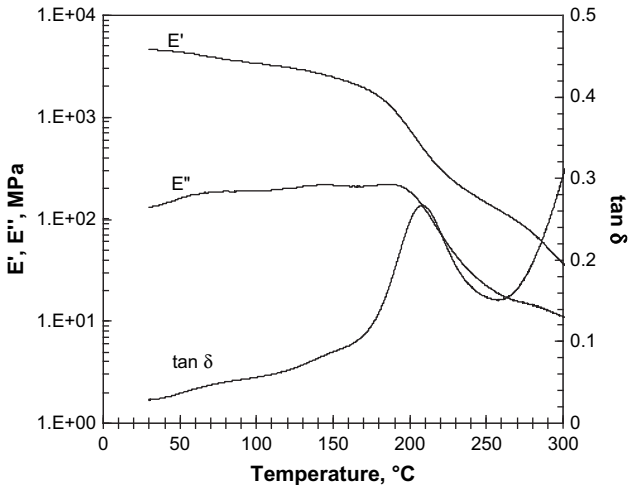


Fig. 5. DMA of poly(P-dds) after 250 °C treatment.

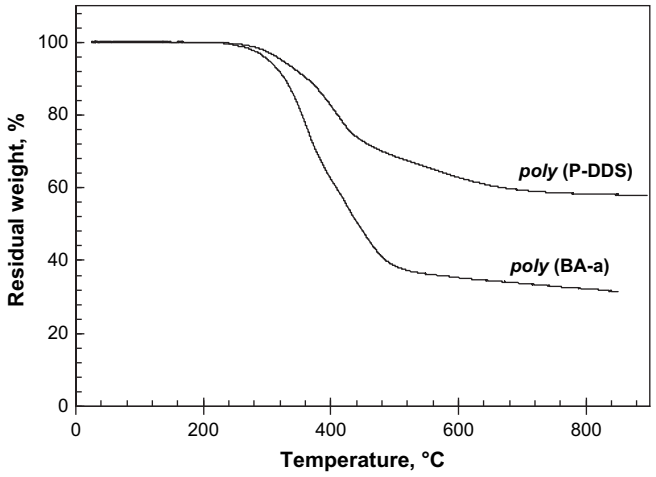


Fig. 6. TGA thermograms of poly(P-dds) and poly(BA-a) under argon atmosphere.

poor resolution of the peak, it is not easy to determine the precise peak position.

While tan δ does not exactly correspond to the T_g position, it is nonetheless used to study T_g especially when the peak position of E'' spectrum is difficult to be determined. The tan δ peak position is observed at 203 °C. The higher glass transition temperature of 203 °C in comparison to that of PBA-a (171 °C) [28] might be due to the higher crosslinking density due to the presence of vacant para position in the phenol part. However, since the rubbery plateau was not observed, it is not possible to evaluate the crosslink density difference.

The thermal stability of DDS-based benzoxazine was studied by TGA. Fig. 6 shows the TGA thermograms of both poly(BA-a) and poly(P-dds). For poly(BA-a), the T_{d5} and T_{d10} are 310 and 327 °C, respectively whereas for poly(P-dds) T_{d5} and T_{d10} increases to 324 and 362 °C, respectively. Also, the char yield of poly(P-dds) is 58%, which is higher than that of poly(BA-a) (32%) by ca. 26%, suggesting the outstanding thermal properties of this diamine-based benzoxazines.

4. Conclusion

DDS-based benzoxazine monomer was prepared for the first time from DDS as a weak aromatic diamine. We have applied the solution method to synthesize the monomer by using a nonpolar solvent such as xylenes at high temperature (150 °C). The purity of the monomer obtained by this novel method was quite high in comparison with that obtained from DMSO. The thermally activated polymerization of the monomers afforded polybenzoxazine characterized by T_g at ca. 203 °C, 10% decomposition temperature of 362 °C and char yield of 58%.

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