

Article

Structure–Property Relationships of Aryl Ether Diamine-Based Benzoxazines: Role of Aromatic Substitution and Molecular Weight Between Crosslinks

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Abstract

A systematic evaluation of meta-substitution and backbone molecular weight in diamine-based benzoxazines was conducted to investigate the impact on melt processability, network development, and the structure–property relationships in polybenzoxazines. Six benzoxazine monomers derived from aryl ether diamines were synthesized, with controlled levels of meta-substitution and varying numbers of ether-bridged phenyl rings in the monomer backbone. Meta-substitution was found to suppress crystallinity in high-purity benzoxazine monomers and lower onsets of polymerization were observed due to meta-positioning of the terminal diamine rings. Terminal diamine meta-substitution also led to higher polymerization enthalpies, attributed to the emergence of an additional polymerization mechanism that increased the glass transition temperature up to 60 °C and delayed the onset of mass loss degradation. Benzoxazines with glass transition temperatures approaching 200 °C are susceptible to Mannich bridge degradation during polymerization, and this additional polymerization pathway both illustrates the nuanced complexities of benzoxazine structure–property relationships as well as provides a potential design strategy for benzoxazines with high glass transition temperatures approaching 250 °C.

Keywords: benzoxazine; crosslinking; substitution effects; isomer; isomerism; structure–property relationships; diamines

1. Introduction

Benzoxazines are a class of modern phenolics that can be synthesized from a wide variety of phenols, amines, and aldehydes. Polymerization proceeds through cationic ring-opening polymerization to form complex thermoset polymers. Several commercial systems are currently available, with target applications ranging from flame-retardant aerospace interiors to tooling materials due to their potential for low flammability, high glass transition temperatures, and low coefficient of thermal expansion. However, there is growing interest in developing high-performance polybenzoxazines for use in structural composites and as precursors to polymer-derived carbon [1]. Specifically, aromatic diamine-based benzoxazines have been demonstrated to possess large, low-viscosity processing windows and produce polymers with high thermal stabilities and char yields. However, complex network formation in model systems, multiple structure-dependent crosslinking pathways, purity-dependent reactivity, and a wide range of reported monomer purities based on synthetic conditions complicate rational monomer design, as reviewed by Lochab et al. [2].



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Subtle variations in monomer structure have been found to result in large, unexpected differences in polymer properties between different isomers [3–5]. These differences arise from a complex combination of hydrogen bonding of chain ends, propagating positions, and additional crosslinking sites.

In contrast to thermosets based on step-growth, addition polymerization results in the presence of chain ends. During benzoxazine addition polymerization, the propagating chain end features a phenolic hydroxyl group and a tertiary amine positioned such that intramolecular hydrogen bonding can occur, leading to the formation of a six-membered hydrogen-bonded ring [6]. These structures form during polymerization and have been shown to stabilize chain ends, effectively capping them and blocking further propagation [7]. As a result of this termination by hydrogen-bonded chain ends, monofunctional benzoxazines cannot produce high-molecular-weight linear polymers [8]. Bifunctional benzoxazines are used to compete against this chain termination to achieve network gelation, but remain highly branched [9]. These chain ends, either the sites of initiation or termination, act as structural defects within the network and are considered to be initial sites for thermal degradation in benzoxazines [10]. Liu et al. found that ortho-substitution disrupts the formation of these hydrogen-bonded chain ends, thereby allowing continued network growth. In contrast, para-substitution promotes hydrogen-bonded ring formation, in some cases to the extent that it severely limits or even prevents polymerization altogether [4].

Benzoxazine polymerization occurs by an electrophilic aromatic substitution process on the imine carbocation intermediate, where the electron-donating or withdrawing character of the phenol precursor influences the benzoxazine C-O bond strength, resulting in a tunable onset temperature of polymerization [11]. Propagation is generally depicted as occurring from the available ortho site of the phenol ring, but many hydrogen-substituted aromatic ring positions can also act as nucleophiles on the imine carbocation during propagation [12,13]. In model phenol or bisphenol A-aniline benzoxazines, substitution occurs primarily at the phenol or bisphenol ortho site due to the donation of electron density from the benzoxazine oxygen, increasing its nucleophilicity. When sites of high nucleophilicity are purposefully blocked by methylation, less nucleophilic positions are instead substituted, albeit at higher activation energies, which illustrates that even in model benzoxazines, a complex distribution of crosslinking species is observed [14,15].

Additional polymerization mechanisms are also enabled based on the benzoxazine monomer structure beyond the addition of traditionally recognized reactive functional groups [2]. Electron-donating substituents such as methyl groups increase the nucleophilicity of available aromatic ring sites within the backbone of benzoxazine monomers, allowing for additional crosslinking functionality [12]. The aromatic substitution pattern has also been shown to influence network formation, where meta-substitution has been shown to enable an additional crosslinking site at the position ortho to the amine in aromatic amine-based benzoxazines [16]. This reactivity is facilitated by electron density donation by adjacent ortho-positioned electronegative atoms, such as oxygen and nitrogen, which increases the acidity of the ortho-positioned hydrogen and allows it to serve as an additional crosslinking site during polymerization [17]. While these additional reactive sites increase network connectivity, their relative contribution to network development is thought to be cure path dependent [12,18].

However, these trends do not always hold true and may directly compete. In bisphenol-based benzoxazines, Ishida reported a 57 °C increase in T_g when moving from para- to ortho-substitution, which was attributed to reduced hydrogen bonding and premature chain termination in the para-substituted system [4]. Kolanadiyil et al. found that meta- and ortho-substituted bisphenol-based benzoxazines had lower T_g values than a para-substituted analogue, with T_g values of 291 °C (para), 270 °C (meta), and 266 °C (ortho) [17].

This decrease was attributed to the formation of aza-cyclic structures and increased network irregularity, leading to greater free volume. In contrast, Sarychev et al. [3] observed a 33 °C increase in T_g for P-34ODA (meta, para) compared to P-44ODA (para, para), while in a subsequent study, Gorbunova reported a 23 °C increase in T_g of P-33DDM (meta, meta) compared to P-44DDM (para, para) [5].

To address these gaps, a systematic study examining the influence of molecular weight between crosslinks and controlled meta-aromatic substitution was conducted in diamine-based benzoxazines. This approach was taken to resolve these aliased factors on structure–property relationships in polybenzoxazines as a handle for controlling high-char-yielding polymers as replacements for phenolics.

In this work, six benzoxazine monomers derived from aryl ether diamines with controlled meta-substitution content and comprising two to four ether-bridged phenyl rings were synthesized and purified. The novel benzoxazines P-133APB and P-1444APPB were synthesized to enable a systematic comparison with P-144APB [19], as well as P-34ODA, P-44ODA, and P-134APB [3]. Their polymerization behavior, as well as the thermal and mechanical properties of the resulting polymers, was characterized and evaluated to provide a fundamental understanding of the effect of aromatic diamine design on polybenzoxazine structure–property–processing relationships.

2. Materials and Methods

2.1. Materials

4,4'-Oxydianiline (98%) (44ODA, Alfa Aesar, Ward Hill, MA, USA), K_2CO_3 (99%) and sodium borohydride (98%) were purchased from Alfa Aesar. 3,4'-Oxydianiline (97%) (34ODA), 1,4-Bis(4-aminophenoxy)benzene (98%) (144APB), and 1,3-Bis(3-aminophenoxy)benzene (98%) (133APB) were purchased from TCI (Tokyo, Japan). 1,3-Bis(4-aminophenoxy)benzene (99.49%) (134APB) and 4,4'-oxydiphenol (99%) were purchased from AmBeed (Arlington Heights, IL, USA). Paraformaldehyde (95%), phenol (99%), 1-fluoro-4-nitrobenzene (99%), and palladium on carbon (10 wt.%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Toluene (ACS grade), dichloromethane (DCM) (ACS grade), acetone (ACS grade), ethanol, tetrahydrofuran (THF), and acetonitrile (HPLC grade) were purchased from Fischer Chemical (Zurich, Switzerland). Dimethyl acetamide (DMAc) (99.5%), 1,4-dioxane (99.8%), 2-hydroxybenzaldehyde 99%, and dimethyl sulfoxide- d_6 (99.9%) were purchased from Thermo Scientific (Waltham, MA, USA). Hydrogen (UHP) was purchased from Southern Gas, and N-Methyl-2-pyrrolidone (NMP) (99.5%) was purchased from Acros Organics (Geel, Belgium) and stored over molecular sieves.

2.2. Measurements

Proton NMR spectra were collected in DMSO- d_6 using a Bruker 400 MHz NMR (Bruker, Billerica, MA, USA). Differential scanning calorimetric (DSC) was performed using aluminum hermetic pans in a Q200 DSC (TA Instruments, New Castle, DE, USA). Samples were heated from room temperature to 300 °C under nitrogen from 2.5 to 10 °C/min for kinetic measurements, and melting, onset, and peak measurements are tabulated at 10 °C/min. Thermogravimetric analysis (TGA) was conducted using high-temperature platinum pans in a Discovery TGA (TA Instruments, New Castle, DE, USA). Samples were heated at 1 °C/min under nitrogen atmosphere. Dynamic mechanical analysis (DMA) was conducted using a Q800 DMA (TA Instruments, New Castle, DE, USA) equipped with a tension film clamp at 1 Hz with a 3 °C/min ramp from room temperature to 300 °C. TGA-MS was collected using a STA 449 F3 Jupiter (NETZSCH Instruments North America, LLC, Burlington, MA, USA) connected to a QMS 505 Aëolos mass spectrometer (NETZSCH Instruments North America, LLC, Burlington, MA, USA). Samples were heated at 20 °C/min from RT to 1000 °C under He.

2.3. DMA Sample Preparation

Monomers were degassed under vacuum at 150 °C, except for P-144APB and P-1444APPB, which required a higher degassing temperature of 190 °C due to their higher melting temperatures. After 30 min, the monomers were poured into preheated silicone molds and placed into a preheated convection oven. The temperature of the oven was ramped at 2 °C/min with a 2 h isothermal hold at 180 °C and a 4 h isothermal hold at 210 °C before allowing to cool naturally.

3. Results and Discussion

3.1. Synthesis of Diamine-Based Benzoxazine Library

Diamine-based benzoxazine monomers, shown in Figure 1, from two- and three-ring diamines were synthesized from the traditional one-pot benzoxazine solution process using diamines, phenol, and paraformaldehyde, followed by column chromatography to remove oligomers. As the amine is bifunctional, an insoluble triazine gel forms rapidly after the addition of paraformaldehyde, which gradually breaks down and converts into the diamine-based benzoxazine. An aryl ether diamine with four aromatic rings in the backbone was not commercially available, so the diamine was prepared according to the procedure reported by Dingemans et al. [20]. The resulting diamine had very low solubility, preventing the benzoxazine from being prepared through the same one-pot method as the other benzoxazines. Because of this, P-1444APPB was prepared according to the three-step method reported by Sarychev et al. [3]. The reaction conditions for all monomers and their precursors are detailed in Sections S1.1–S1.6 in the Supporting Information. The structures and purity were confirmed by the ^1H NMR shown in Figure 2. In particular, the lack of additional methylene peaks or shoulders adjacent to the oxazine methylene peaks at 4.6 and 5.4 ppm is evidence of a lack of ring-opened oligomer species.

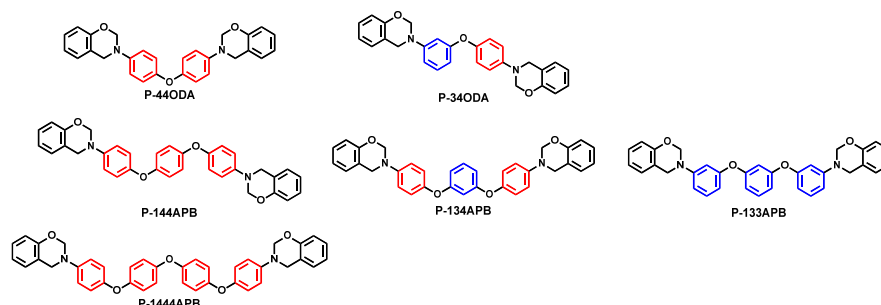


Figure 1. Diamine-based benzoxazine library. Red: Para substitution, blue: meta substitution.

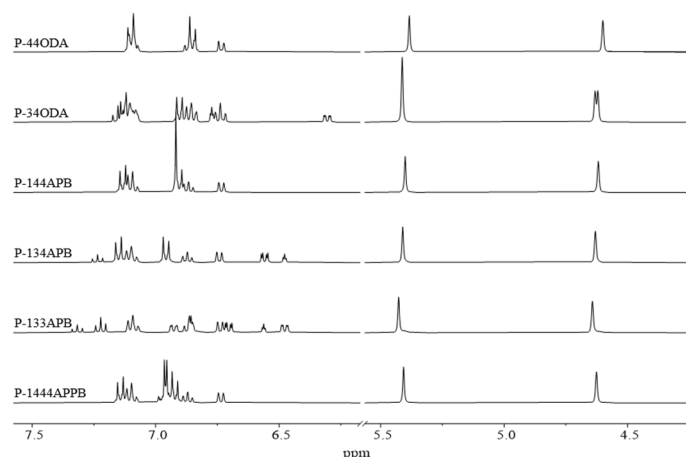


Figure 2. ^1H NMR spectra of benzoxazine monomers.

3.2. Polymerization Behavior

High melting temperatures pose a challenge for liquid-based part manufacturing techniques such as resin transfer molding or prepreg processing. While all para-substituted monomers, P-44ODA, P-144APB, and P-1444APPB, were crystalline solids at room temperature, meta-substitution disrupted crystallization for meta-substituted counterparts, P-34ODA, P-134APB, and P-133APB, as shown in Figure 3. For the all-para-substituted homologous series, as molecular weight increased, an increase in melting temperature was observed, which is hypothesized to be due to an increase in intermolecular forces within the crystalline lattice.

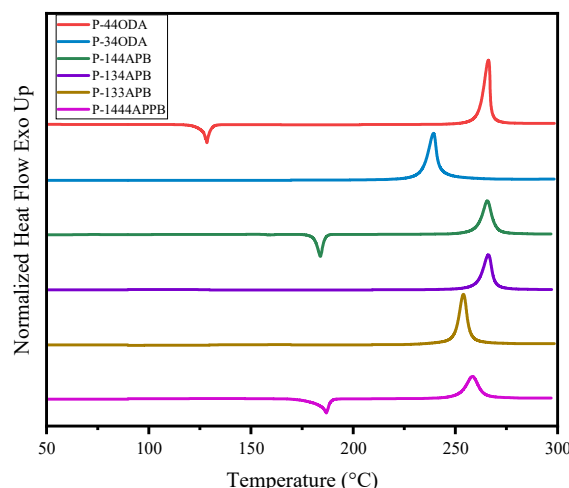


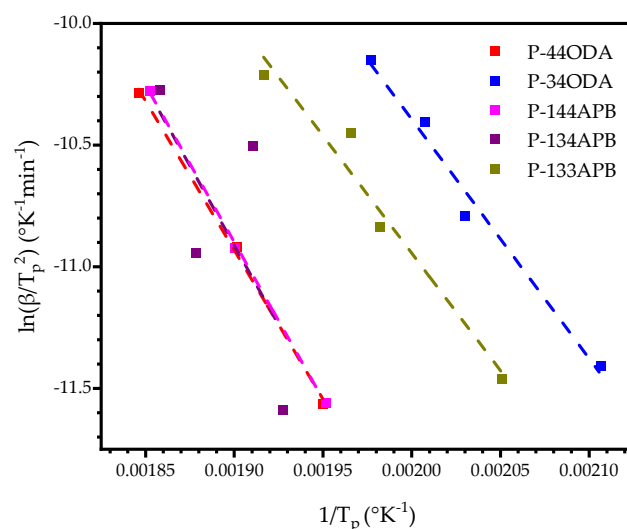
Figure 3. Thermograms of benzoxazine diamine isomer library at 10 °C/min.

The onset of monofunctional benzoxazine polymerization is known to be modified by amine nucleophilicity, where increased amine electron density stabilizes the imine carbocation intermediate, leading to higher onsets of polymerization [21]. This influence was observed both by Sarychev et al. and Kolanadiyl et al. as higher temperature onsets of polymerization for an all-para-substituted oxydianiline diamine-based benzoxazine in comparison to mixed meta-para counterparts [3,17]. This is due to electron density donation by the aryl ether linkage when substituted para to the amine by resonance. When considering substitution effects in diphenyl methane diamine-based benzoxazines, Gorbunova et al. found no influence of ring substitution on polymerization onset, but this may have been due to the comparatively lower electron-donating capacity of the methylene linkage relative to that of an aryl ether [5].

The monomers with exclusively para-phenoxy substituted amines had nearly identical onset and peak polymerization temperatures, shown in Figure 3 and listed in Table 1, for P-44ODA, P-144APB, and P-134APB. Lower onset and peak polymerization temperatures were observed in the monomers with meta-phenoxy substituted amines (P-34ODA and P-133APB), in agreement with the findings of Sarychev and Kolanadiyl [3,17]. The only outlier among the para-substituted group was P-1444APPB, which displayed a slightly lower polymerization temperature. This is likely due to its inability to be additionally purified by column chromatography, stemming from low solubility due to high molecular weight and extended conjugation. Reaction kinetics were calculated using a Kissinger plot, shown in Figure 4, where the increased reactivity due to meta positioning of the aryl ether linkage in the terminal rings of the diamine was observed as a roughly 20 kJ/mol lower activation energy of polymerization in Table 1 for P-34ODA and P-133APB relative to P-44ODA, P-144APB, and P-134APB.

Table 1. Tabulated diamine benzoxazine thermal and kinetic properties.

Monomer	T _{melt} (°C)	T _{onset} (°C)	T _{peak} (°C)	ΔH _{Polymerization} (J/g)	E _a (kJ/mol)
P-44ODA	128	261	266	312	102
P-34ODA	-	234	239	385	81.8
P-144APB	184	261	265	258	108
P-134APB	-	261	266	258	109
P-133APB	-	250	254	350	80.3
P-1444APPB	186	252	258	223	-

**Figure 4.** Kissinger plot of benzoxazine diamine isomer library.

3.3. Polymer Properties

DMA was used to investigate the thermal and mechanical properties of polybenzoxazines. For the fully para-substituted series, as the number of ether-bridged phenyl rings in the benzoxazine backbone increased, both the storage modulus and T_g decreased either by the onset of the storage modulus or the peak in tan delta due to a higher molecular weight between crosslinks, as shown in Figure 5 and Table 2. The storage modulus in the rubbery state is proportional to crosslink density, where a continual decrease in the rubbery modulus was observed as the molecular weight between crosslinks increased. The lack of a stable rubbery plateau in P-44ODA, P-144APB, and P-1444APPB is due to the low thermal stability of the Mannich bridge in the polybenzoxazine network, which has been shown to cleave as low as 225 °C [22–24]. This low-temperature degradation prevents networks from reaching complete cure. Despite this well-documented degradation pathway, it is often overlooked in the literature. Many high-T_g polybenzoxazines are subjected to cure cycles above 225 °C, resulting in networks that are no longer composed of ideal polybenzoxazine structures but instead contain complex fractions of degradation products. In some systems, the extent of degradation is significant enough to produce an additional peak in the tan delta curve at around 260 °C, corresponding to an increase in the storage modulus.

Meta-substitution was found to increase both the glass transition temperature (T_g) and rubbery modulus, as shown in Figure 6, when comparing the two-ring backbone benzoxazines P-34ODA (meta, para) and P-44ODA (para, para). A T_g increase of over 60 °C and a more than doubling of the rubbery modulus was observed, as listed in Table 2. As the rubbery plateau modulus is proportional to crosslink density, this behavior is hypothesized to arise from the introduction of additional crosslinking functionality. Possible additional crosslinking topologies are illustrated in Scheme 1.

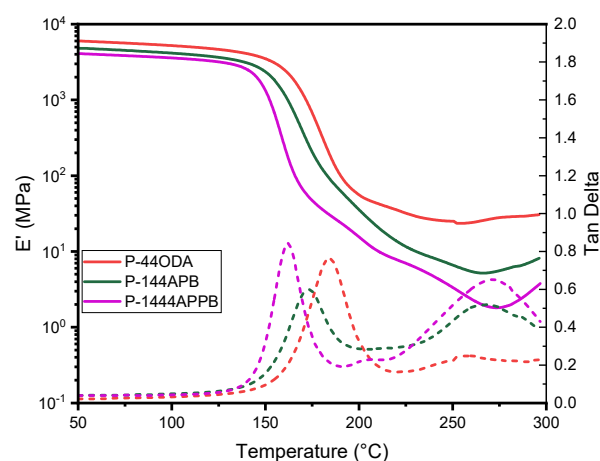


Figure 5. Storage modulus (solid lines) and tan delta (dashed lines) from DMA of polybenzoxazines with increasing backbone molecular weight.

Table 2. TGA summary of polybenzoxazine powders with a 1 °C/min ramp to 1000 °C under nitrogen purge. Rubbery storage modulus values taken at T_g by peak tan delta + 40 °C.

Monomer	T_g (°C) E' Onset	T_g (°C) Peak Tan Delta	Rubbery Modulus (MPa)
P-44ODA	154	183	23.5
P-34ODA	225	243	65.3
P-144APB	150	173	18.1
P-134APB	140	163	133
P-133APB	192	210	88.0
P-1444APPB	145	160	14.5

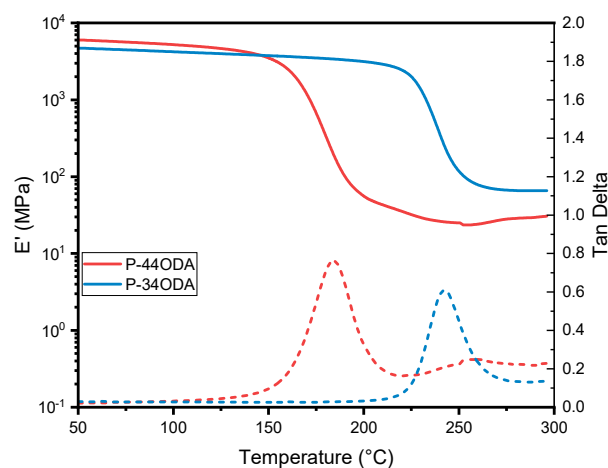
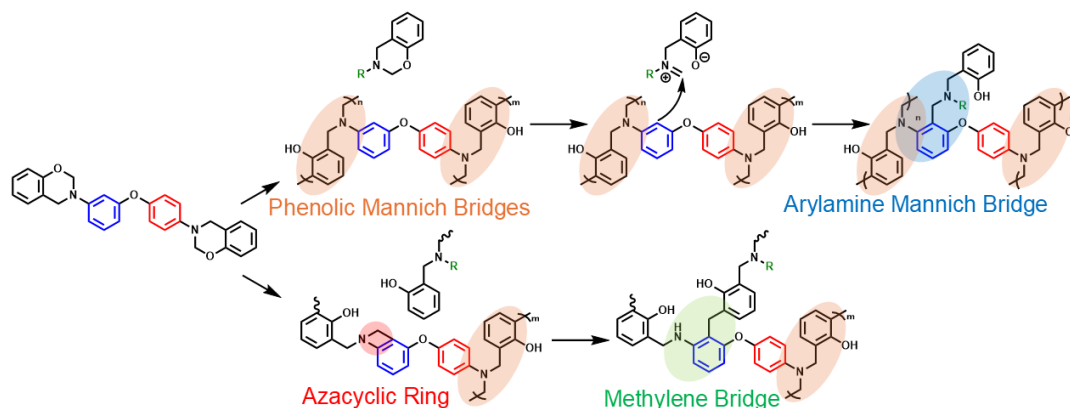


Figure 6. Storage modulus (solid lines) and tan delta (dashed lines) from DMA of polybenzoxazines with two aromatic rings in the backbone and varying meta/para-substitution.

Electron-donating substituents are known to enable participation of many additional aromatic ring positions to function as additional nucleophiles during benzoxazine ring opening. This results in the formation of arylamine Mannich crosslinks, which are thought to be more rigid than traditional phenolic Mannich bridges due to the removal of the comparatively more flexible dimethylene-substituted tertiary amine linkages [12]. Sites of increased electron density, such as the aromatic ring position ortho to the amine and aryl ether linkage found solely in the meta-substituted terminal diamine rings found in P-34ODA and P-133APB, have been hypothesized to lead to this arylamine crosslinking off of the backbone of the diamine [3]. Additionally, the meta-N,O motif of the meta-aryl ether

substitution on the terminal rings of the diamines in this work is also thought to form an azacycle of N-methylene benzazetidines on opening of the adjacent benzoxazine. These azacycles have been shown to form during benzoxazine polymerization and are thought to then undergo further ring opening, leading to additional crosslinks with aromatic rings positioned ortho to phenolic hydroxyls [16].



Scheme 1. Potential additional polymerization mechanisms enabled by meta-substituted aryl ether linkages on the terminal position of the amine. R denotes any potential benzoxazine backbone. **Top:** Participation of the diamine backbone aromatic substitution as a nucleophile during benzoxazine polymerization. **Bottom:** Azacyclic route displaying N-methylene benzazetidine formation and then azacycle ring opening leading to methylene bridge crosslinking with available phenolic hydroxyls [3,12,17].

A similar observation in T_g was found with the three-ring backbone diamine-based benzoxazines between P-134 (para, meta, para) and P-133 (meta, meta, meta), as shown in Figure 7 and Table 2. Additionally, a greater than fivefold increase in the rubbery modulus was observed between that of P-144APB (para, para, para) and P-134APB (para, meta, para). Interestingly, Kolanadiyil identified meta-substitution specifically of the amine and ether as necessary to activate an additional crosslinking position, where P-144APB and P-134APB only contain para-substituted amines and ethers in the monomer structures [17]. This indicates that the central ring in P-134APB, with meta-substituted aryl ether linkages, may become activated in an analogous manner, which would be expected as the aryl ethers are electron-donating.

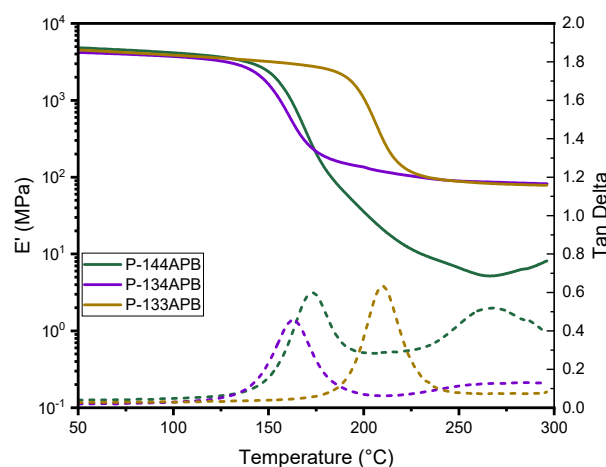


Figure 7. Storage modulus (solid lines) and tan delta (dashed lines) from DMA of polybenzoxazines with three aromatic rings in the backbone and varying meta/para-substitution.

The thermal degradation behavior of the polybenzoxazines was investigated by TGA. As the number of aromatic rings in the benzoxazine backbone increased, as shown in Figure 8, the temperature corresponding to 5 wt.% mass loss ($T_{5\%}$) increased while the final char yield decreased, as tabulated in Table 3. The phenolic Mannich crosslink is known to be the least thermally stable moiety in aromatic benzoxazine networks [23]. Consequently, as the molecular weight of the benzoxazine monomers increases, the relative mass fraction of this thermally labile linkage decreases, resulting in a higher onset temperature for thermal degradation. However, the accompanying increase in ether-bridge heteroatom content with increasing ring number in the monomer backbone reduces the char yield due to a relative reduction in aromatic carbon content.

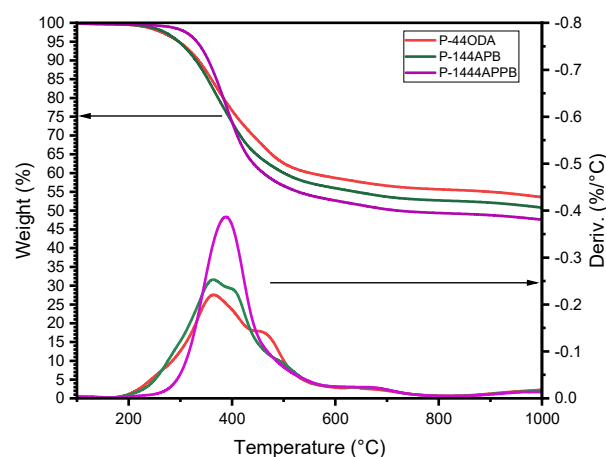


Figure 8. Derivative of mass loss and weight percent vs. temperature for all-para-benzoxazine networks from TGA runs at 1 °C/min in nitrogen atmosphere.

Table 3. TGA summary of polybenzoxazine powders with a 1 °C/min ramp to 1000 °C under nitrogen purge.

Monomer	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char Yield at 1000 °C (wt.%)
P-44ODA	303	344	53.5
P-34ODA	331	353	57.6
P-144APB	306	337	50.7
P-134APB	312	343	51.3
P-133APB	341	368	46.3
P-1444APPB	337	360	47.6

Meta-substitution was also found to increase thermal stability in the two-ring backbone benzoxazines P-34ODA (meta, para) and P-44ODA (para, para), where a higher temperature onset of mass loss and higher char yield was observed, as shown in Figure 9. In the three-ring backbone benzoxazines, a marginal difference in char yield was observed between P-134APB and P-144APB, while P-133APB had a 4.4 wt.% lower char yield compared to P-144APB, as shown in Figure 10. Onsets of mass loss degradation trended similarly to the two-ring benzoxazines. All onsets of mass loss and char yields are tabulated in Table 3. Interestingly, the three-ring P-133APB displayed the highest onset temperature of degradation, even higher than the two-ring P-34ODA, indicating a potential tradeoff in thermal stability based on the relative concentrations of the traditional phenolic Mannich bridge crosslink and the additional crosslinks shown in Scheme 1, which is notable as the arylamine crosslinks have been found to have higher thermal stability [12].

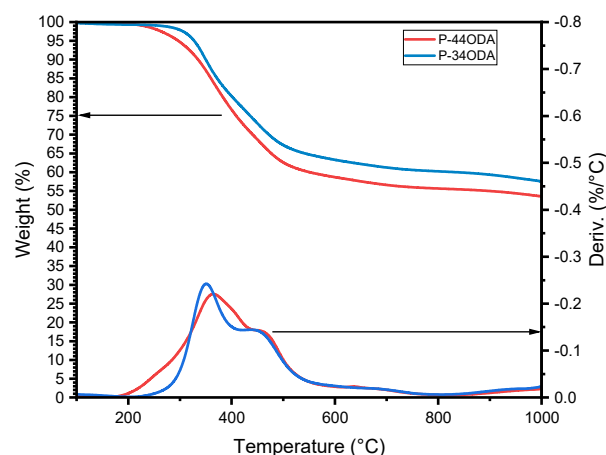


Figure 9. Derivative of mass loss and weight percent vs. temperature for two-ring benzoxazine networks from TGA runs at 1 °C/min in nitrogen atmosphere.

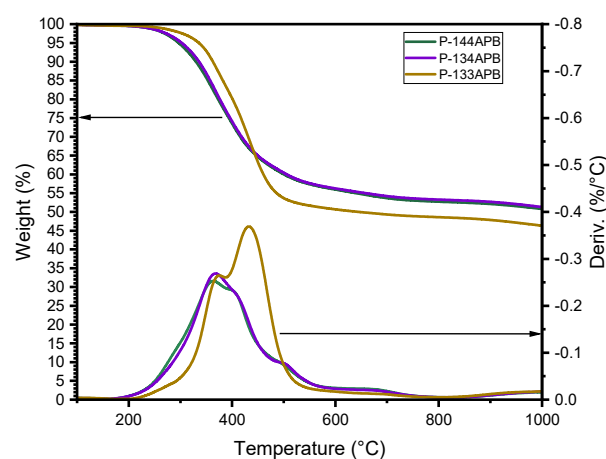


Figure 10. Derivative of mass loss and weight percent vs. temperature for three-ring benzoxazine networks from TGA runs at 1 °C/min in nitrogen atmosphere.

Simply comparing char yield, which reflects the retention of condensed-phase species during pyrolysis, does not account for differences in elemental composition among the monomers. To address this, it is often more informative to evaluate “carbon yield”, which normalizes char yield to the theoretical carbon content of the starting monomer. Carbon yield was determined by assuming that the residual mass at 1000 °C consists entirely of carbon and calculating the ratio of the theoretical carbon content of the monomer to the measured char yield. This provides a metric for conversion efficiency, where an ideal material would retain all carbon atoms during pyrolysis, resulting in a carbon yield of 100%. As shown in Figure 11 for the all-para series, as the molecular weight increased, carbon conversion efficiency decreased as the lower crosslink density allowed more volatilization of low-molecular-weight species from the degrading network. The additional crosslinking mechanism increased the carbon yield between the two-ring backbone benzoxazines P-44ODA and P-34ODA. A similar trend was observed in the three-ring systems between P-144APB and P-134APB, but a large drop was observed in P-133APB. It is hypothesized that the meta-substitution of the central ring in P-133APB leads to an additional degradation mechanism, resulting in volatilization of resorcinol-based degradation products.

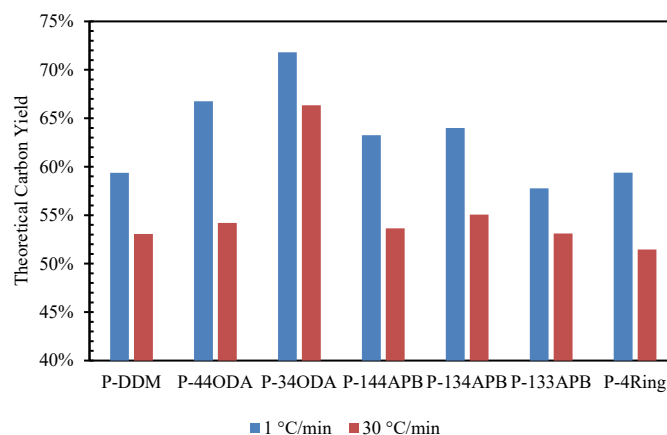


Figure 11. Carbon yield of diamine-based polybenzoxazines.

4. Conclusions

Structurally similar benzoxazine monomers based on aryl ether diamines with varying meta-substitution and molecular weight were successfully synthesized and characterized. Larger-molecular-weight benzoxazine backbones decreased the glass transition temperature but delayed the onset of mass loss degradation due to a lower concentration of the less thermally stable phenolic Mannich crosslinks. Meta-substitution of the diamines was hypothesized to enable an additional crosslinking site, leading to higher glass transition temperatures and onsets of degradation. The additional crosslinking site does not appear limited to the terminal rings of the aromatic amine, and in the case of P-133APB, it was also hypothesized to occur from the 2-position of the central di-aryl ether flanked ring.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18040440/s1>, Section S1.1: Synthesis of P-44ODA; Section S1.2: Synthesis of P-34ODA; Section S1.3: Synthesis of P-144APB; Section S1.4: Synthesis of P-134APB; Section S1.5: Synthesis of P-133APB; Section S1.6: Multistep Synthesis of P-1444APPB; Figure S1: ^1H NMR of P-1444APPB.

Author Contributions: Conceptualization, C.D.; methodology, C.D. and A.H.; formal analysis, C.D. and A.H.; investigation, C.D. and A.H.; resources, J.W. and C.D.; data curation, C.D.; writing—original draft preparation, C.D. and A.H.; writing—review and editing, A.H.; visualization, C.D. and A.H.; supervision, J.W.; project administration, C.D.; funding acquisition, J.W. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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