Synthetic Strategies to Combine High Performance Benzoxazine Thermosets with Polymers

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Summary: Polybenzoxazines are newly developed thermosetting polymers exhibiting versatility in a wide range of applications including electronics and aerospace industries. They exhibit highly competitive combination of properties compare to the conventional thermosets. In this paper we present synthetic strategies to incorporate thermally curable benzoxazine functions into polymers as main and side chain groups in order to further improve various properties. The strategies successfully employed include monomer synthesis, macromonomer method, polycondensation, oxidative polymerization, photo-polymerization, click chemistry and hydrosilylation processes. In the case of macromononomer method functional initiators were used in various controlled/living polymerizations to give polymers with benzoxazine end groups. The thermal curing behaviors of the obtained polymers were also demonstrated.

Keywords: benzoxazine; cross-linking; main and side chain functional polymers; thermoset

Introduction

Polybenzoxazine based materials have gained much interest in the field of thermosets because of superior properties that overcome several short-comings of conventional novolac and resole-type phenolic resins. These materials offer several advantages including low water absorption, high char yield, resistance against flame, high modulus, high strength, and high glass transition temperatures (T_g). Their synthesis is a thermally induced self polymerization reaction of precursor 1,3-benzoxazines which takes place without any initiator or curing agent (Scheme 1). The curing process of conventional thermosets is usually accompanied with a large volume shrinkage causing serious concerns such as creation of internal stress, voids and cracks in the cured resin. Low dimensional shrinkage during curing reaction of benzoxazines arising from the ring-opening reaction is a striking feature of benzoxazine based polymers.[1–2]

Though polybezoxazines have a variety of superior properties, pure polybenzoxazine based polymers also suffer from some problems, namely, (i) high curing temperature (~200 °C or higher), (ii) difficulty in processing and (iii) brittleness.[3] In particular, except some examples,[4–5] most of the monomers are usually powder and processing into thin films is rather difficult. The formed polymers are generally brittle as a consequence of the low molecular weight of the network structure. The conventional strategies to overcome these disadvantages are the preparation of benzoxazine monomers with additional functionality and blending with a high-performance polymer or filler and fiber.[6–11] Another promising strategy is the synthesis of novel polymeric precursors which are designed so as to impart processibility and flexibility properties. In this paper we describe synthetic strategies to prepare main- and side-chain benzoxazine functional polymers by taking advantage of monomer synthesis, various polymerization

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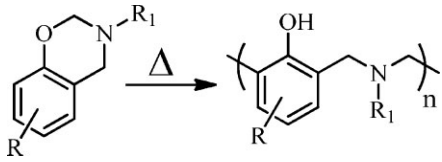


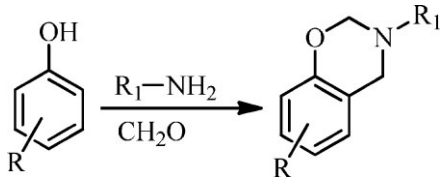
Scheme 1.
Thermally induced ring opening polymerization of 1,3-benzoxazines.

methods, and click chemistry approach. Before discussing these strategies, it is essential to present the characteristics of the monomer synthesis as it is of general use in the synthesis main-chain polymers and monomers possessing suitable additional functionality for the subsequent polymerization processes.

Synthesis of Benzoxazine Monomers

1,3-Benzoxazines were first synthesized by Cope and Holly in 1940 s[12] by using primary amines, formaldehyde and phenol, however the ring opening polymerization potency of benzoxazines has been recognized much later.[13–15] Though the synthesis of benzoxazine monomers by using various types of phenols and primary amines is easy (Scheme 2), selection of starting compounds is an important restriction on the yield. For example, presence of electron withdrawing functional groups (-CO_2H, -CN etc.) on phenols or primary amines was found to be responsible for decreases in the yield of the reaction. Also, it is hard to synthesize benzoxazine monomers containing free phenolic -OH groups employing conventional one-pot method.[16–18]

Tailoring the benzoxazine monomer by using judiciously chosen phenol and amine



Scheme 2.
Synthesis of 1,3-benzoxazines.

the curing process and properties of resulting thermosets can be designed. As an example, additional polymerizable sites were attached to benzoxazine monomers to obtain highly crosslinked materials having high T_gs.[19–20]

Despite the synthesis of benzoxazine using phenols, formaldehyde and primary amines is quite convenient and cost effective some other alternative routes have also been reported such as (i) use of 1,3,5-triphenylhexahydro-1,3,5-triazine as active intermediate,[1] (ii) step-wise preparation of benzoxazines from imines[21] (iii) by *ortho*-lithiation of phenols, followed by reaction with $ZnBr_2$ and *N,N*-bis[(benzotriazol-1-yl)methyl][22] etc.

Side-Chain Precursors

Side chain functionalization is an elegant way to incorporate benzoxazine groups into a polymer backbone to achieve a highly dense network. There are various synthetic methods to obtain such polymers. Some include post-polymer modification like click chemistry or polymerizing monomers possessing benzoxazine molecules. For example, bifunctional monomers containing both methacrylate[23] or maleimide[24] and benzoxazine functionalities were synthesized. These functional groups undergo sequential polymerization by free radical and thermally activated ring opening reactions, respectively. Both monomers were readily copolymerizes with styrene by photochemical means using a photoinitiator such as ω,ω-dimethoxy-ω-phenylacetophenone (Scheme 3).

In this step, the photochemical method was deliberately chosen so as to retain thermally active side-chain benzoxazine units. In the case of maleimide functional monomers, perfectly alternating copolymers were obtained as a consequence of the formation of charge transfer complex between strong electron donating and accepting monomers. The processable copolymers formed this way can be thermally cured to yield thermosets with excellent thermal stability.

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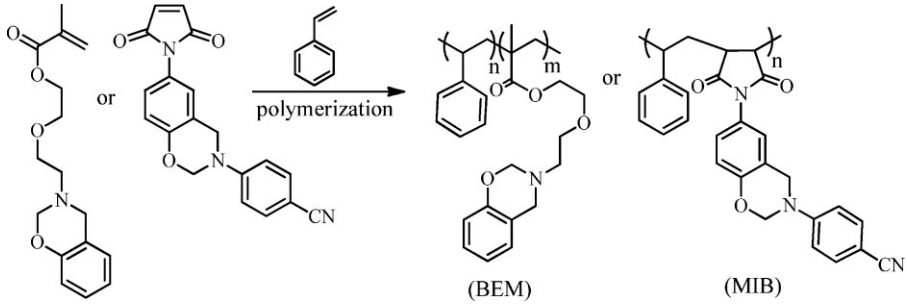
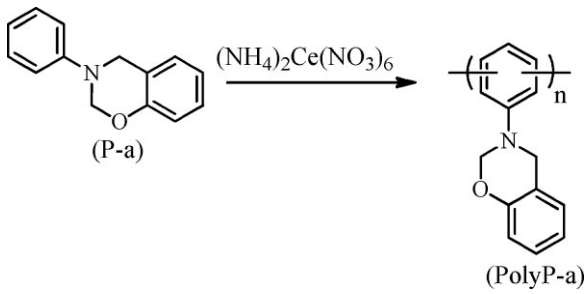


Scheme 3.
Copolymerization of benzoxazine methacrylates or maleimides with styrene.

Another side-chain polymeric benzoxazine precursor (PolyP-a) was prepared by oxidative polymerization 3-phenyl-3,4-dihydro-2H-benzo[e][1,3] oxazine (P-a) in the presence of ceric ammonium nitrate [25]. It was noted that the conjugated polymers partly contain ring opened structures as a consequence of the acidic medium. However, this phenolic ring opened structures contribute positively as catalyst and influence the curing kinetics. The resulting polymers exhibit conductivities around 10^{-2} S cm^{-1} and undergo thermal curing at various temperatures. The cured products exhibited high thermal stability but lower conductivity than those of the precursors. The oxidative polymerization was also applied to copolymerize with thiophene eventually yielding thermosets with extremely high thermal stability.

Post polymer modification was also applied to incorporate benzoxazine moieties to several polymers such as PVC, polystyrene and polybutadiene by using "Click Chemistry".[26–28] Typical example concerns the preparation of polystyrene-benzoxazine (PSt-B) with well defined structure and functionality. For the synthesis of parent azide functionalized polymer, we first poly(styrene-*co*-chloromethylstyrene) P(St-*co*-CMSt) was prepared via nitroxide mediated radical polymerization of styrene and chloromethylstyrene at 125 °C.

Approximately 40% of chloro groups of P(St-*co*-CMSt) were converted to azido groups by using NaN_3 in *N,N*-dimethylformamide. Propargyl benzoxazine was prepared independently by a ring closure reaction between *p*-propargyloxy aniline, paraformaldehyde, and phenol. Finally, azidofunctionalized polystyrene was coupled to propargyl benzoxazine. The overall synthetic pathways are represented in Scheme 5. The subsequent thermal curing process was then conducted in the usual manner. The polymers cured in this way exhibited much more thermal stability



Scheme 4.
Oxidative polymerization of benzoxazine monomer (P-a).

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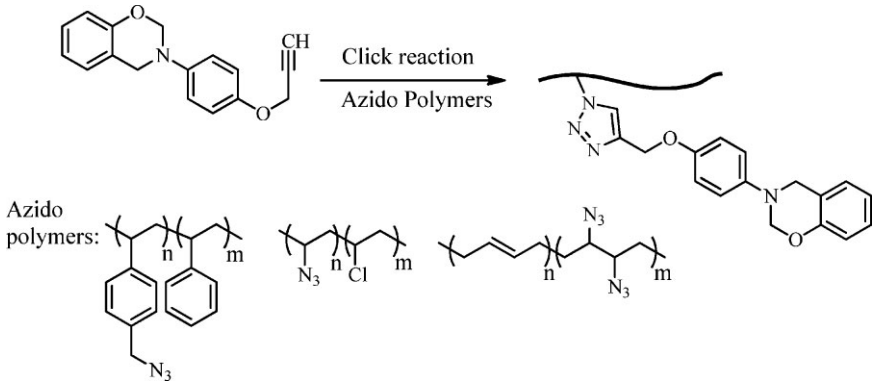

Scheme 5.
Benzoxazine grafting to various polymers via Click Chemistry.

than polystyrene cross-linked beads prepared by the conventional method.

In this connection it is worth to mention the work of Nagai *et al.* [29] who synthesized polymers having benzoxazine moieties in the main chain by using similar click reaction. Difunctional *N*-propargyl benzoxazine was efficiently used with *p*-xylene-α,α'-diazide in the presence of Cu(I) catalyst to form the corresponding linear polycondensate having 1,2,3-triazole junctions. Moreover, Chernykh *et al.* have reported the preparation of linear high molecular weight polymers containing benzoxazine in the main chain by applying click reaction by utilizing a novel azide-containing benzoxazine monomer.[30] These polymers possess molecular weights significantly higher than the benzoxazine polymers which have been obtained by Mannich reaction and found to be between 20,000 and 40,000 Da.

Main-Chain Precursors

One of the most interesting questions about benzoxazine chemistry is how the high molecular weight affects the apparent reactivity of benzoxazine in the ring opening reaction. Obviously, besides potential processability and film forming properties, highly crowded benzoxazine units present in the main chain may alter the polymerization behavior as well as the properties of the cured product due to highly dense network structure. The nature of the back bone could play an important role. For the preparation of such main chain polymers monomer synthesis, polycondensation, click chemistry and hydrosilylation processes. Takeichi and Ishida have independently reported a synthetic approach for the preparation of polymers containing benzoxazine moieties in the main chain.[31–32] They adopted the monomer synthesis as the method of obtaining high-molecular weight polybenzoxazine precursors by using aromatic or aliphatic diamine, bisphenol-A and paraformaldehyde (Scheme 6).

This type of Mannich polymerization produced polymers with rather low molecular weights and partially ring-opened structures were observed. However, the ratio of the ring-closed structure in the precursor was enough to be used as polybenzoxazine precursors. The toughness and the tensile strength of the crosslinked polybenzoxazine films were enhanced compared to the cured film from the typical benzoxazine monomers. Particularly, polybenzoxazine from aromatic diamines exhibited the highest strength and modulus among polybenzoxazine precursors.

In this main chain precursor context, we have synthesized high molecular weight poly(etheresters) (PEE) containing benzoxazine units in the main chain using the diol functional benzoxazine monomer and

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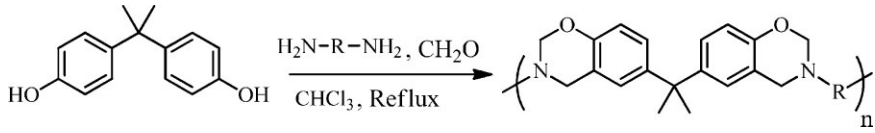


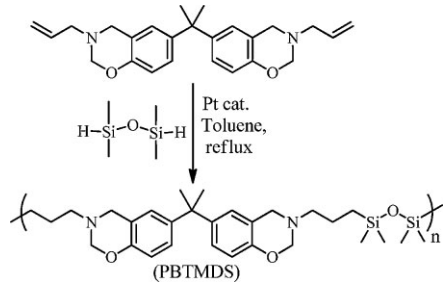
Scheme 6.
Synthesis of polybenzoxazine precursors.

diacid chlorides namely adipoyl and terephthaloyl chlorides[33] (Scheme 7). Polycondensation of these reagents resulted in corresponding PEE-A (adipoyl based) and PEE-T (terephthaloyl based) with molecular weights around 34,000 Da.

Transparent flexible thin films of these reactive poly(etherester)s were obtained by solvent casting method. Films were further cross-linked thermally and the flexibility was retained depending on curing conditions. The cured PEE exhibited good thermal stability and toughness, induced by the soft ether and ester groups.

We have also reported oligosiloxanes containing thermally curable benzoxazine units, namely poly(benzoxazine tetramethyldisiloxane) (PBTMDS) in the main chain that they were prepared by hydrosilylation reaction between tetramethyldisiloxane and benzoxazine having allyl groups[34] (Scheme 8).

Although the chain growth is limited and only oligomers are formed, it is clear that the process is highly selective and the products exhibit the properties of both

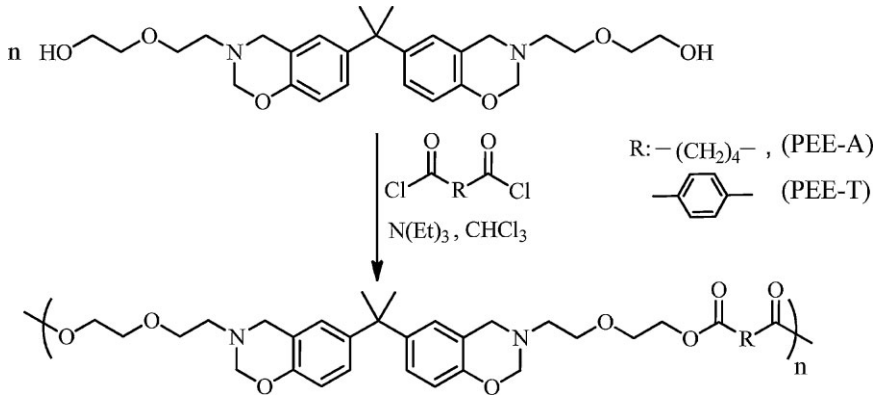


Scheme 8.
Synthesis of oligosiloxanes containing thermally curable benzoxazines.

segments. Siloxane segments introduce flexibility and transparent thin precursor films were easily obtained by solvent casting. Cured polymers exhibited much more thermal stability than those of allyl functional benzoxazine. The enhanced thermal stability was attributed to the presence of siloxane units.

Benzoxazine Functional Telechelic Polymers

Telechelic polymers are defined as macromolecules that contain reactive end-groups



Scheme 7.
Synthesis of poly(etheresters) containing benzoxazine units in the main chain.

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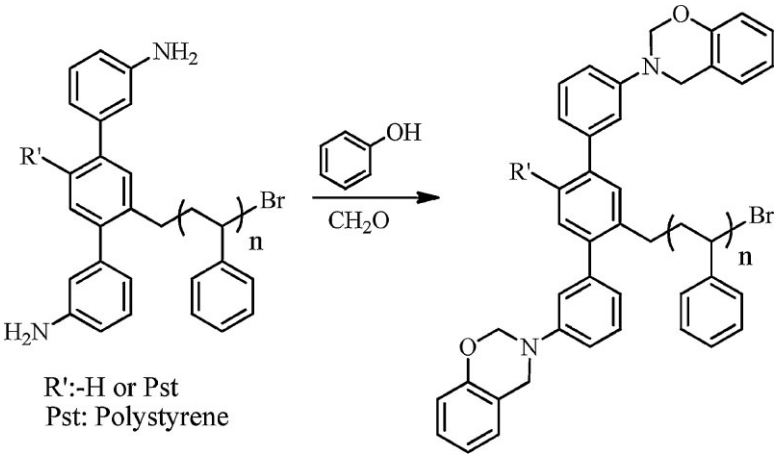
that have the ability to react selectively with another molecule. Depending on the functionality, telechelics can be classified as mono-, di-, tri-, and multifunctional telechelics (polytelechelics). Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers.

By using telechelic approach, benzoxazine ring has been anchored to the end of various polymers. We have reported a unique synthetic route for the synthesis of a benzoxazine attached PSt macromonomer (PSt-B macromer).[35] First, dibromophenyl terminated polystyrene was synthesized using Atom Transfer Radical Polymerization (ATRP) and by a following Suzuki coupling reaction, amino functional polymer was prepared. These amino functional polymers were reacted with phenol and paraformaldehyde to produce benzoxazine functionalized polystyrene macromonomers (Scheme 9).

It was shown that miscible blends of polybisbenzoxazine and poly(ε-caprolactone) (PCL) can be prepared by an in situ curing reaction of benzoxazine in the presence of PCL due to the intermolecular hydrogen bonding between the hydroxyl groups of polybisbenzoxazine and the carbonyl groups of PCL.[36] Accordingly, we have synthesized naphthoxazine ring containing PCL macromonomers (PCL-Na) by using alcohol functional naphthoxazine as initiator for ring opening polymerization of ε-caprolactone. Hence, thermosets of polybenzoxazines with covalently bonded PCL segments were formed by curing PCL macromonomers with conventional benzoxazine monomers (see Scheme 10).

Addition to previous example, other thermally curable naphthoxazine-functionalized polymers were synthesized by the reaction of linear (diamines) and branched (triamines) poly(propylene oxide)s (PPO-Na) (Jeffamine series) having various molecular weights, with paraformaldehyde and β-naphthol (Scheme 11). Properties and morphologies of the products before and after curing were investigated.[37]

Moreover, benzoxazines were used as an alternative photo-initiating system for methyl methacrylate in the presence of thioxanthone based photo-sensitizers.[38] In these experiments, benzoxazines behaved as a hydrogen donor in the presence of aromatic carbonyl photo-sensitizers in photo-initiated free radical polymerization. The initiation action of benzoxazine begins with an electron transfer and a following hydrogen abstraction from Ar-CH_2-N part of oxazine ring, which results in the formation of a benzoxazine radical analo-



Scheme 9.
Synthesis of benzoxazine attached polysterene macromonomers.

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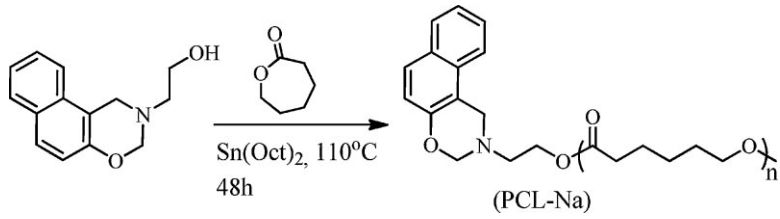


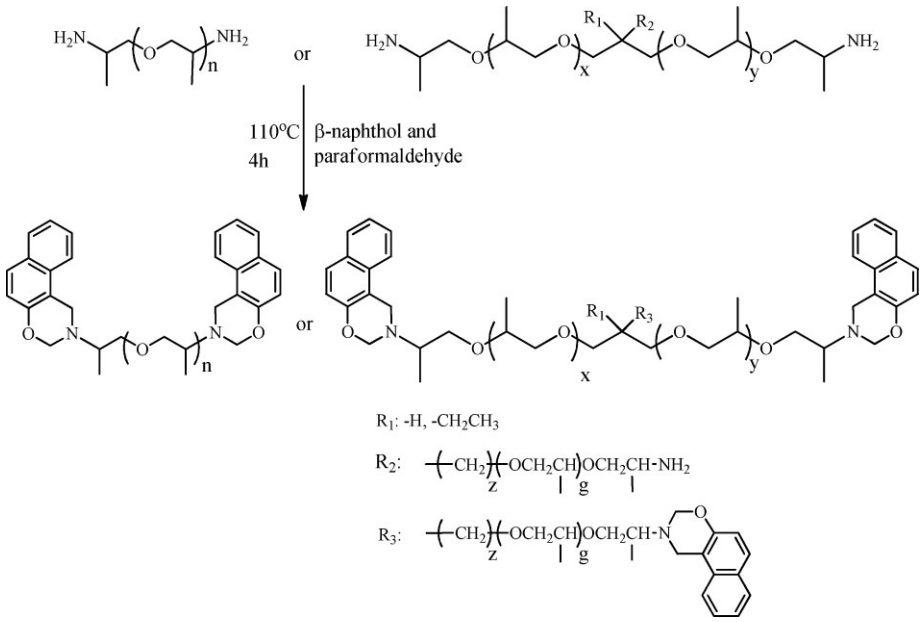
Scheme 10.
Synthesis of naphthoxazine ring containing PCL macromonomer.

gous to thioxanthone/amine systems. It was observed that efficient photo-initiation of free radical polymerization using benzoxazines was achieved at wavelengths around $\geq$350 nm (see Scheme 12).

Interesting network structures can be obtained from benzoxazine macromonomers since these macromonomers undergo thermal curing alone or with added benzoxazines which can form domains of macromolecules hanging as dangling chains. Considering the preparation of a self supported film using a benzoxazine monomer has been difficult, one of the important characteristics of such telechelics is their ability to cast films easily.

Thermal Properties

The thermal decomposition and curing characteristics of the benzoxazine containing polymers are listed in Table 1. The maximum curing temperatures generally depends on the number of benzoxazine units in the polymer structure. Therefore, in telechelic systems, high curing temperatures can be explained by dilution of benzoxazines, since the possibility of the collusion of benzoxazine units decreases drastically. Additionally, polymers having some ring opened benzoxazines reveals curing maximums below 220 °C by the effect of free phenolics, as the acidic conditions decrease the ring opening tem-



Scheme 11.
Synthesis of naphthoxazine-functionalized poly(propylene oxide).

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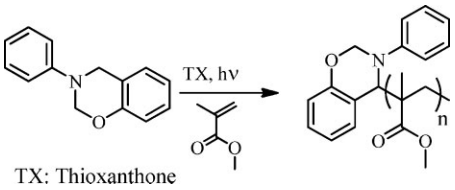

Scheme 12.
Synthesis of benzoxazine end chain poly(methyl methacrylate).

Table 1.
The molecular weights, thermal decomposition and curing characteristics of the benzoxazine containing polymers.

Polymer	M_n[a] (GPC)	Maximum Curing Temperature (°C)	Char Yields at 800 °C (%)
MIB	3750	280	38[b]
BEM	8900	257	46
PolyP-a	19100	203	75
PSt-B	13500	250	36
PVC-B	63000	218	58
PB-B	15620	199	43
PEE-A	33400	250	22
PEE-T	33700	240	36
PBTMDS	2530	247	61
PSt-B macromer	4270	271	nd[c]
PCL-Na	9890	nd[c]	nd[c]
PPO-Na	2000	251	nd[c]

[a]Determined according to polystyrene standards.
[b]Char yield at 600 °C.
[c]Not determined.

peratures of benzoxazines. PolyP-a is an example for this phenomena, because of the oxidative polymerization conditions the polymer contains some ring opened benzoxazines.

Generally, degradation of polybenzoxazines starts with Mannich base cleavage around 350 °C and then phenolic decomposition can be observed at around 450–500 °C. Finally, thermal aromatization and cross-linking during degradation lead to char formation. Char yields of the corresponding polymers in Table 1 clearly show that incorporation of benzoxazines into polymeric structures increases the char formation compared to non-benzoxazine containing relevant polymers. For example, benzoxazines containing PVC has 58% char yield at 800 °C. This is an approximately 10 folds enhancement compared to commercial PVC which has only 5% char yield at 800 °C. Similarly, benzoxazine containing polystyrene has 36% char yield at 800 °C where polystyrene beads are completely evaporates.

Conclusion

In the present paper, synthetic strategies for the preparation of a series of benzoxazine functional macromonomers, main- and side-chain benzoxazine polymers were presented. Each method has been discussed in terms of ease of the procedure, molecular weight and side reactions. The thermal curing behavior of the polymers strongly depends on the polymer structure and concentration of benzoxazine units. The ring opened ring structures which may form during the synthetic process also influence the thermally activated curing process.

The synthetic approaches presented here may serve a valuable guideline for preparing high performance thermosets with desired and predetermined properties especially useful for industrial applications. Since the final properties of the resulting thermosets obtained from the various compositions with monomeric benzoxazines can be tuned by an appropriate selection of the polymer, one should expect further development of such synthetic methods.

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