

# Benzoxazine Containing Polyester Thermosets with Improved Adhesion and Flexibility

ALEV TUZUN,<sup>1</sup> BARIS KISKAN,<sup>1</sup> NESLIHAN ALEMDAR,<sup>2</sup> A. TUNCER ERCIYES,<sup>2</sup> YUSUF YAGCI<sup>1</sup>

<sup>1</sup>Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

<sup>2</sup>Department of Chemical Engineering, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

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**ABSTRACT:** High molecular weight polyesters containing thermally curable benzoxazine units in the main chain have been synthesized. For this purpose, first the diol functional monomer is synthesized through the Mannich and subsequent ring closure reactions of bisphenol-A, paraformaldehyde, and 5-amino-1-pentanol. Polycondensation of the resulting benzoxazine and pyromellitic dianhydride or 4,4'-(hexafluoroisopropylidene) diphthalic anhydride with or without dibutyltin laurate yielded the corresponding polyesters with the molecular weights between 5800 and 7000 Da. The structures of the precursor diol monomer and the resulting polyesters are confirmed by Fourier transform infrared spectroscopy and proton nuclear magnetic resonance spec-

troscopy analysis. Curing behavior of both the monomer and polymers has also been studied by differential scanning calorimetry. Flexible films of the polyesters were obtained by solvent casting on tin plates and crosslinked by heating in the absence of any catalyst. The cured films exhibited high flexibility and adhesion on the tin plates as determined by ASTM and DIN tests. Thermal properties of the cured polymers were also investigated by thermogravimetric analysis (TGA). © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 4279–4284, 2010

**KEYWORDS:** adhesion; benzoxazine; crosslinking; curing; flexibility; high performance; polybenzoxazine; thermoset

**INTRODUCTION** Polybenzoxazines are relatively new class of materials, which are alternative to phenol formaldehyde resins. They have a good combination of attractive properties, such as (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) high  $T_g$ , in some cases higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, and (vi) release of no by-product during curing.<sup>1</sup> The cured materials also possess thermal and flame retarding properties of phenolics along with better mechanical performance. The striking feature is connected with dimensional stability during the conversion from monomer to polymer because of the ring opening nature of the polymerization. In fact, the polymerization occurs through thermal activation of the corresponding benzoxazines without any catalyst and without generating any by-products (see Scheme 1).<sup>2–6</sup>

Moreover, benzoxazine monomers can be prepared simply from inexpensive and commercially available phenols, primary amines, and formaldehyde.<sup>5,7–9</sup> Therefore, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using appropriate starting materials and polybenzoxazine properties can be tailored. Polybenzoxazines prepared from the monomer precursors form some limitations on their use in practical applications. The monomers are usually powder and processing into thin films is rather difficult. Additionally, the formed polymers are brittle as a consequence of the short molecular weight of the network

structure. To overcome these limitations various approaches were proposed. These include (i) synthesis of specially designed novel monomers,<sup>10–18</sup> (ii) blending with polymers or fillers and fibers,<sup>19–21</sup> or (iii) synthesis of end-chain, side chain, or main-chain polybenzoxazines.<sup>22–29</sup> In spite of the significant improvements on some properties, the desired flexibility and adhesion could still not be achieved. Aiming at expanding their industrial applicability it seemed appropriate to prepare a family of highly flexible benzoxazine polycondensates tailored to meet different requirements, depending on the specific application. Our working concept is based on creating polymeric backbones integrating segments that induce molecular flexibility and adhesion on metals on one hand, and that comprise thermally curable benzoxazine moieties on the other hand. This article describes synthesis, characterization, and thermal curing of polyesters containing benzoxazine moieties in the main chain from diacid anhydrides and diol containing bisbenzoxazines. As will be shown, the obtained polymers exhibit an enhanced adhesion and flexibility even after thermal curing.

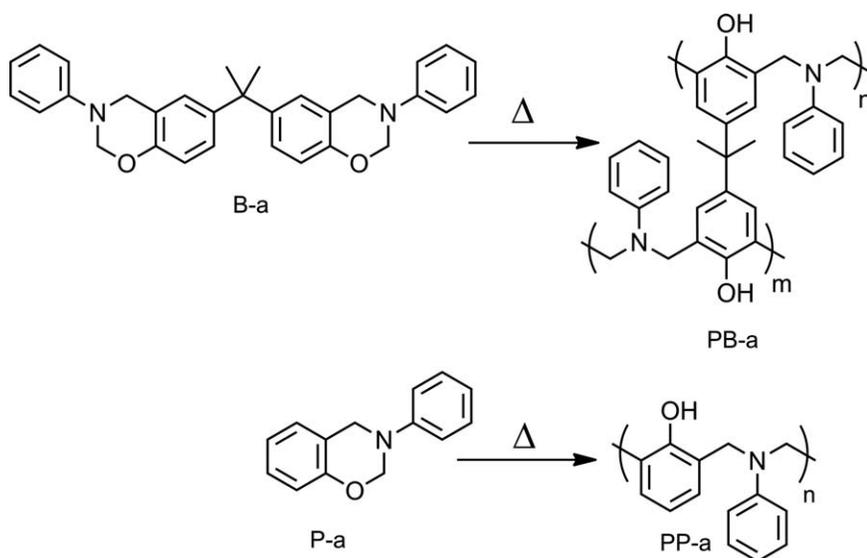
## EXPERIMENTAL

### Materials

4,4'-Isopropylidenediphenol (Acros, 97%), paraformaldehyde (J.T. Baker, 95%), 5-amino-1-pentanol (Aldrich, 97.0%), 1,4-dioxane (Riedel-de Haën 99.5%), sodium hydroxide (Carlo

Correspondence to: Y. Yagci (E-mail: yusuf@itu.edu.tr)

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**SCHEME 1** Thermally activated ring opening polymerization of mono- and bisbenzoxazines.

Erba, 97%), anhydrous magnesium sulfate (Alfa Aesar, 99.5%), chloroform (Riedel-de Haën, 99.4%), pyromellitic dianhydride (Merck, 97%), *N,N*-dimethylformamide (Merck, 99.8%), dibutyltin laurate (Aldrich, 95.0%), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (Aldrich, 99.0%) were used as they received.

### Characterization

Proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) spectra were recorded in deuterated chloroform with tetramethylsilane as an internal Standard, using a Bruker AC250 instrument at a proton frequency of 250.133 MHz. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer via attenuated total reflectance technique with  $4\text{ cm}^{-1}$  resolution and 20 scans and for each sample. Differential scanning calorimetry (DSC) experiments were performed on Perkin-Elmer Diamond DSC with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under nitrogen flow ( $20\text{ mL}/\text{min}$ ). Thermogravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under nitrogen flow ( $200\text{ mL}/\text{min}$ ). Molecular weights were determined against polystyrene standard using size exclusion chromatography (GPC) equipped with a Waters 1515 pump and Waters styragel column (HT4) using DMF containing  $5\text{ mM NH}_4\text{PF}_6$  at a flow rate of  $0.5\text{ mL}/\text{min}$ .

### Synthesis of Bisbenzoxazine-Diol

Synthesis of diol functional bisbenzoxazine was performed according to the following procedure. To  $150\text{ mL}$  of 1,4-dioxane, paraformaldehyde ( $176\text{ mmol}$ ,  $5.3\text{ g}$ ), 5-amino-1-pentanol ( $88\text{ mmol}$ ,  $9.08\text{ g}$ ), and 4,4'-isopropylidenediphenol ( $44\text{ mmol}$ ,  $10\text{ g}$ ) were added and refluxed for 3 days. Then, 1,4-dioxane was evaporated under vacuum. Oily raw product was dissolved in chloroform and washed five times with  $25\text{ mL}$   $0.2\text{ N}$  NaOH aqueous solution and distilled water, respectively. The chloroform solution was dried with anhydrous magnesium sulfate, filtered and evaporated under vacuum to afford orange-yellow oil. (Yield: 62%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta =$

$1.39\text{ (m, 4H, N-CH}_2\text{-CH}_2\text{-CH}_2\text{)}$ ,  $1.42\text{ (m, 4H, N-CH}_2\text{-CH}_2\text{)}$ ,  $1.57\text{ (s, 6H, isopropylidene -CH}_3\text{)}$ ,  $1.63\text{ (m, 4H, HO-CH}_2\text{-CH}_2\text{)}$ ,  $2.73\text{ (broad t, 4H N-CH}_2\text{)}$ ,  $3.60\text{ (broad t, 4H HO-CH}_2\text{)}$ ,  $3.69\text{ (broad s, 2H, OH)}$ ,  $3.91\text{ (s, 4H, oxazine Ar-CH}_2\text{-N)}$ ,  $4.80\text{ (s, 4H, oxazine, O-CH}_2\text{-N)}$ ,  $6.65\text{--}6.95\text{ (6H, aromatics)}$ .

### Synthesis of 4-(2H-1,3-benzoxazin-3(4H)-yl)Benzoic Acid

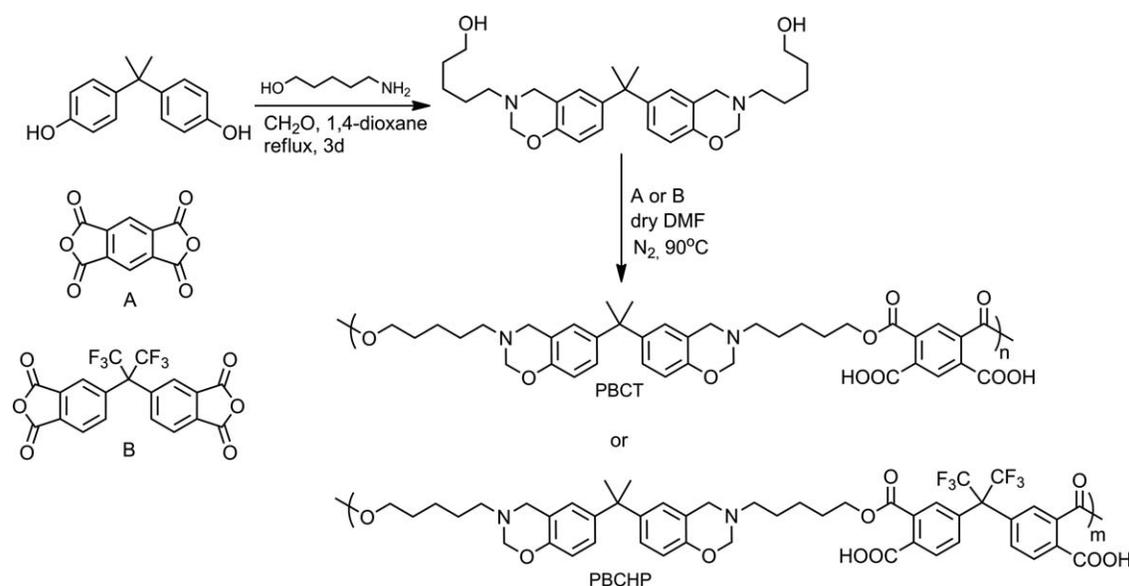
A mixture of phenol ( $5.0\text{ g}$ ,  $53\text{ mmol}$ ), 4-aminobenzoic acid ( $7.0\text{ g}$ ,  $51\text{ mmol}$ ), and paraformaldehyde ( $3.2\text{ g}$ ,  $105\text{ mmol}$ ) was placed in a  $500\text{-mL}$  round-bottom flask and  $200\text{ mL}$  of 1,4-dioxane was added to this mixture. The mixture was refluxed, and the reaction was monitored with thin layer chromatography ( $20:1$  dichloromethane/ethanol) until the initial product disappeared (5 days). After cooling to room temperature, the mixture was filtered and concentrated by evaporating  $4/5$  of 1,4-dioxane at rotary evaporator. Ethyl ether ( $150\text{ mL}$ ) was added to the mixture with magnetic stirring, and a yellow precipitate was obtained. The yellow solid was filtered and dried under reduced pressure. (Yield: 50%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 4.81\text{ (s, 2H, N-CH}_2\text{-Ar)}$ ,  $5.57\text{ (s, 2H, N-CH}_2\text{-O)}$ ,  $6.78\text{--}7.84\text{ (m, 8H, aromatics)}$ ,  $12.45\text{ (broad s, 1H, COOH)}$ .

### Synthesis of 3-Phenyl-3,4-dihydro-1,3-benzoxazine (P-a Monomer)

P-a monomer was prepared via typical solventless method.<sup>30</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 4.49\text{ (s, 2H, N-CH}_2\text{-Ar)}$ ,  $5.37\text{ (s, 2H, N-CH}_2\text{-O)}$ ,  $6.79\text{--}7.30\text{ (m, 9H, aromatics)}$ .

### Synthesis of Benzoxazine Containing Polyesters

Typical procedure: To  $45\text{ mL}$  of dried DMF, BBD ( $3.9\text{ mmol}$ ,  $1.89\text{ g}$ ), and 1,2,4,5-benzene-tetracarboxylic-1,2:4,5-dianhydride ( $3.9\text{ mmol}$ ,  $0.85\text{ g}$ ) were added and refluxed under  $\text{N}_2$  ( $\text{g}$ ), at  $90\text{ }^\circ\text{C}$  for 24 h. At the end of the reaction, polymer was precipitated in  $500\text{ mL}$  of water and washed with methanol. Then, the polymer was dried under vacuum over two nights. Same procedure was applied for the catalytic reactions except that two drops of dibutyltinlaurate were added to the mixture.



**SCHEME 2** Synthesis of BBD and polyesters.

### Determination of Adhesion and Flexibility Properties of Films

The samples were dissolved in DMF in 1:1 (w/w) solid to solvent ratio. The resulting viscous solutions were applied on tin plates by using an automatic film applicator to obtain 40  $\mu\text{m}$  films. These films obtained from monofunctional benzoxazine P-a, 4-(2H-1,3-benzoxazin-3(4H)-yl)benzoic acid (BBA), and benzoxazine containing polyesters were cured at 160  $^{\circ}\text{C}$  for 1 h and at 170  $^{\circ}\text{C}$  for 2 h, respectively. The adhesion<sup>31</sup> and flexibility<sup>32</sup> properties of films thus obtained were determined according to the related standards.

## RESULTS AND DISCUSSIONS

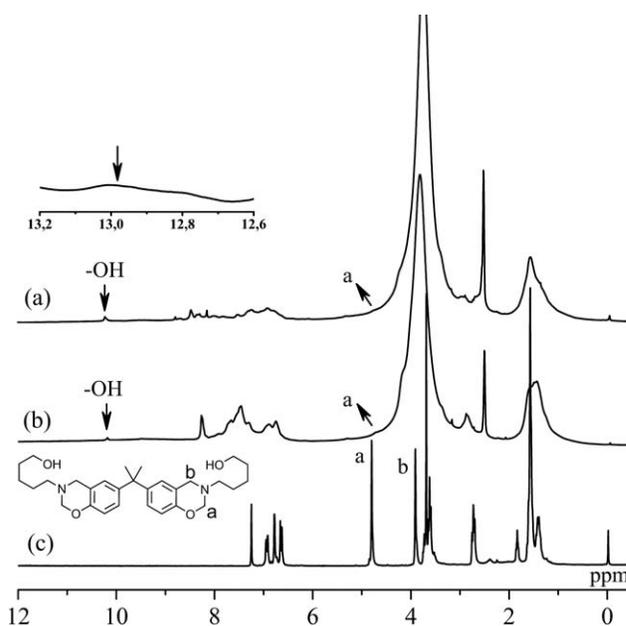
Polyesters are one of the most important and widely used polycondensates. Depending on the nature of monomers, polyesters exhibit an enormous variety of structures, properties, and therefore, applications. Thus, the polyester properties are governed by the design and synthesis of suitable monomers. In our work, we selected aminoalcohol group as the primary amine component in the benzoxazine ring forming reaction to introduce hydroxyl groups in the final benzoxazine. Hence, diol containing benzoxazine was synthesized as the monomer for the subsequent polyesterification process by reacting bisphenol-A, 5-amino-1-pentanol, and paraformaldehyde as depicted in Scheme 2.

The structure was confirmed by spectral and thermal analysis. As can be seen from Figure 1(c) the  $^1\text{H}$  NMR spectrum of the monomer exhibits not only the specific signals of the benzoxazine ring but also chemical shifts that belong to the alkyl chain and hydroxyl groups.

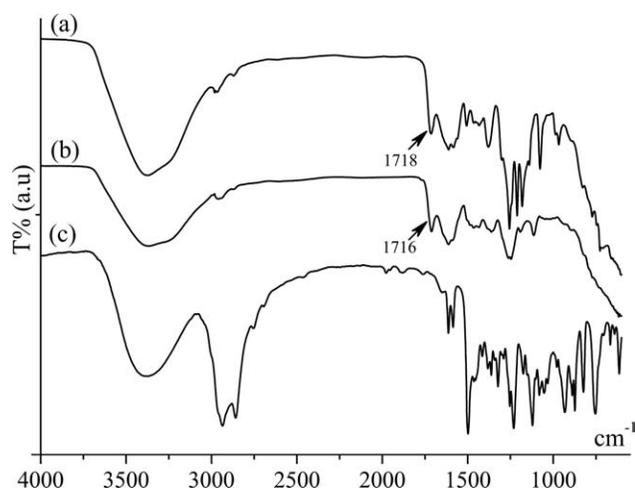
Moreover, the FTIR spectrum of the diol monomer further indicates the structure. As can be seen from Figure 2(c), addition to the band corresponding to the C—O—C oxazine ring mode at 1382  $\text{cm}^{-1}$  and broad aromatic C—H stretching

vibration around 3010  $\text{cm}^{-1}$ , the O—H and C—O (primary alcohol) stretching bands at 3391 and 1054  $\text{cm}^{-1}$ , respectively, were observed. Furthermore, the band at 932  $\text{cm}^{-1}$  is the mode that arises from the benzene ring to which oxazine ring is attached.<sup>33</sup>

It is well known that 1,3-benzoxazines polymerizes with thermal induction around 200–250  $^{\circ}\text{C}$  and exhibit exotherm, which can be monitored by DSC. The thermogram in Figure 3(a) reveals a ring opening exotherm with an onset at 182  $^{\circ}\text{C}$  and a maximum at 210  $^{\circ}\text{C}$ , and 31 J/g as the exothermic energy. Notably, a degradation process begins after 249  $^{\circ}\text{C}$ .



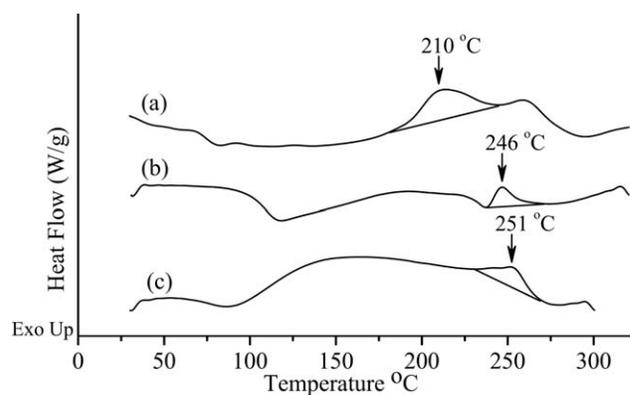
**FIGURE 1**  $^1\text{H}$  NMR spectra of PBCT (a), PBCHP (b), and BBD (c).



**FIGURE 2** FTIR spectra of PBCT (a), PBCHP (b), and BBD (c).

Polyesters can be synthesized by various routes. Conventionally, under appropriate conditions diols can react either with diacid chlorides, diacids, or dianhydrides to form polyesters. For our convenience, pyromellitic dianhydride and 4-4'-(hexafluoroisopropylidene) diphthalic anhydride were used as the dianhydride components to obtain desired carboxylic acid containing polyesters (Scheme 2). The polymerization reactions were performed without or with catalyst (dibutyltin laurate) at 90 °C. Because of the nature of the reaction, in every repeating unit there occurred two molecules of carboxylic acid adjacent to benzoxazine units. This is an important restriction for the preservation of the benzoxazine rings as acids readily undergo ring opening reaction with benzoxazines. In fact, this issue could be monitored spectrally and also by thermal characterization using DSC. The results of the polymerizations are given in Table 1. In our experiments, the amount of dibutyltin laurate, a Lewis acid catalyst, was deliberately kept low so as to prevent ring opening reaction of benzoxazine.

The  $^1\text{H}$  NMR spectra for polyesters were evaluated to confirm the structures. The  $^1\text{H}$  NMR spectrum of the polyesters, namely poly(benzoxazine-carboxyterephthalate) (PBCT) and poly(benzoxazine-carboxyhexafluoro isopropylidene phthalate) (PBCHP), derived from pyromellitic dianhydride and 4-4'-(hexafluoroisopropylidene) diphthalic anhydride, are shown in Figure 1(a,b), respectively. The spectra reveal the characteristic peaks assigned to methylene protons ( $\text{O}-\text{CH}_2-\text{N}$ ) of the oxazine ring at 4.76 ppm for both poly-



**FIGURE 3** DSC traces of BBD (a), PBCHP (b) and PBCT (c).

mers with low intensity, which indicates the ring opening of oxazine during polymerization. Same issue is also evidenced by the peaks of phenolic  $\text{OH}$  protons at 10.2 ppm. Moreover,  $\text{COOH}$  protons of polyesters appeared at 12.9 ppm and the methylene protons of  $\text{Ar}-\text{CH}_2-\text{N}$  could not be detected due to the overlapping with  $-\text{O}-\text{CH}_2$  protons of ester and broad water peak of  $d_6$ -DMSO.

The structure of the both polyesters was also confirmed by FTIR. Figure 2(a,b) shows the IR spectra of the polyesters. The characteristic carbonyl stretching vibrations were observed at 1718 and 1716  $\text{cm}^{-1}$  for PBCT and PBCHP, respectively. In addition, the respective  $\text{COOH}$  stretching vibrations of the polyesters at 3367 and 3373  $\text{cm}^{-1}$  are emerged as broad bands. Also,  $\text{C}=\text{O}$  stretching vibration modes of carboxylic acid are detectable at 1613 and 1612  $\text{cm}^{-1}$ , respectively. DSC was used for characterizing the curing behavior of the polyesters (Fig. 3). As stated previously, benzoxazine groups are expected to undergo ring opening polymerization. This exothermic event was detected for both polymers. PBCT exhibited an onset at 231 °C and a maximum at 251 °C with 15 J/g of exotherm energy. Similarly, for poly(benzoxazine-*co*-carboxy hexafluoroisopropylidene phthalate), the onset of the exotherm started at about 236 °C with a maximum at 246 °C, and 10 J/g as the heat of polymerization. Expectedly, both polymers resembled almost the same thermal properties as they are structurally similar and every repeating unit contains one benzoxazine unit. The slight difference observed for the amount of exotherm is probably due to aliphatic and aromatic nature of the components. The thermal stabilities of the both polyesters are

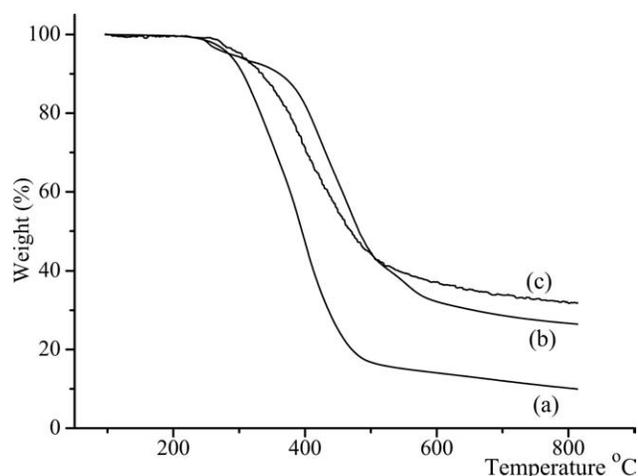
**TABLE 1** Polycondensation of BBD<sup>a</sup> with Anhydrides in DMF at 90 °C

Polyester	Anhydride ( $\text{mol L}^{-1}$ )	Tin Laurate ( $\text{mol L}^{-1}$ )	Conversion <sup>b</sup> (%)	$M_n^c$	$M_w/M_n$
PBCT	$8.6 \times 10^{-2}$	–	64	5,800	1.54
PBCT	$8.6 \times 10^{-2}$	$8.4 \times 10^{-4}$	68	4,700	1.62
PBCHP	$8.6 \times 10^{-2}$	–	66	5,900	2.45
PBCHP	$8.6 \times 10^{-2}$	$8.4 \times 10^{-4}$	69	6,500	2.46

<sup>a</sup>  $8.6 \times 10^{-2} \text{ mol L}^{-1}$ .

<sup>b</sup> Determined gravimetrically based on anhydrides.

<sup>c</sup> Determined by GPC according to the polystyrene standards.



**FIGURE 4** TGA thermograms of cured BBD (a), cured PBCT (b), and PBCHP (c).

similar. The comparative TGA curves are illustrated in Figure 4 and the results are summarized in Table 2.

Cured PBCT exhibited slightly higher char yield due to the rigid aromatic group in the structure imparted by terephthalate group. Interestingly, the thermal degradation of this polymer occurs faster in 315–515 °C temperature range than cured PBCHP. Although they possess COOH groups in the structure, which may undergo decarboxylation, the char yields of cured polyesters are higher than that of cured diol monomer. In fact, this value is even comparable with that of PP-a, which has a 34% char at 800 °C. The observed enhancement in the thermal stability can again be attributed to the aromatic groups and increased crosslink density through additional hydrogen bonding.

The film forming property of the polyesters were also investigated. The adhesion and flexibility of the cured films were measured by ASTM and DIN tests<sup>31,32</sup> and compared with that of the cured conventional monofunctional benzoxazine (Pa) and carboxylic acid containing benzoxazines, BBA (see Schemes 1 and 3, respectively for the structures). In each case, the films from the corresponding compounds were prepared on tin plates and thermally cured at 170 °C for 2 h. In the case of cured P-a and BBA, the films were very brittle and adhesion were very poor. Cracks were formed even by

**TABLE 2** Thermal Properties of the Cured Bisbenzoxazine-Diol and the Polyesters

Cured Polymer <sup>a</sup>	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{max}$ (°C)	$Y_c$ (%)
BBD	285	305	394	10
PBCT	301	334	419	32
PBCHP	285	361	426	27

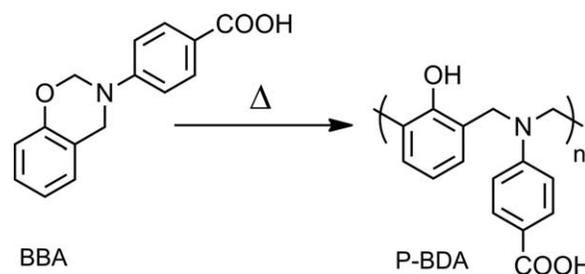
<sup>a</sup> Cured in TGA at 220 °C for 15 min under N<sub>2</sub> stream (20 mL/min).

$T_{5\%}$ : The temperature for which the weight loss is 5%.

$T_{10\%}$ : The temperature for which the weight loss is 10%.

$Y_c$ : Char yields at 800 °C under nitrogen atmosphere.

$T_{max}$ : The temperature for maximum weight loss.



**SCHEME 3** Curing of 4-(2H-1,3-benzoxazin-3(4H)-yl)benzoic acid (BBA).

bending over the cylinder having 20 mm diameter and the adhesions were found to be low. The poor flexibility and adhesion is due to the lacking of film forming property and rigid structure of the network.

In contrast, the polyester samples showed good flexibility and adhesion. The films showed no crack even upon bending over the cylinder having 2 mm diameter and the adhesion were found to be 5B for both polyester samples. The linear chain segments having pentyl and ester groups provide the flexibility in the network. Also, hydroxyl and carboxylic acid groups promote the adhesion of molecules to metals. In Table 3, adhesion values of the low molar mass structurally related model benzoxazines and polyesters were tabulated.

In conclusion, novel polyesters containing benzoxazine moieties in the main chain were synthesized and characterized. Two kinds of polyesters with the molecular weights between 5800–7000 Da were readily obtained by polycondensation of bisbenzoxazine-diol with pyromellitic dianhydride and 4-4'-(hexafluoroisopropylidene)diphthalic anhydride. Flexible thin films were formed by solvent casting on tin plates and further crosslinked by thermally activated ring opening reaction of the benzoxazine groups present in the main chain. The cured polyesters exhibited comparable thermal stability with respect to low molar mass analogous. They also showed high flexibility induced by the soft pentyl and esters groups. Moreover, these cured films showed striking adhesion on tin plates because of the phenolic hydroxyls and carboxylic acid groups. The synthetic strategy presented may open new pathway to prepare other thermoplastic elastomers that can thermally be cured in the absence of any catalyst leading to materials with improved properties. Further studies in this line are in progress.

**TABLE 3** Adhesion of Various Thermally Cured<sup>a</sup> Benzoxazines

Benzoxazine	Adhesion
P-a	2B
P-BBA	2B
PBCT <sup>b</sup>	5B
PBCHP <sup>b</sup>	5B

<sup>a</sup> Cured at 170 °C for 2 h.

<sup>b</sup> Polymers obtained with or without catalyst.

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