NÖHÜ Müh. Bilim. Derg. / NOHU J. Eng. Sci., 18 (2026), 1916858
Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi
Niğde Ömer Halisdemir University Journal of Engineering Sciences
Araştırma makalesi / Research article
www.dergipark.org.tr/tr/pub/ngumuh / www.dergipark.org.tr/en/pub/ngumuh

Synthesis and investigation of the thermal properties of dihydroxyl-functionalized benzoxazine polyesters

Dihidroksil fonksiyonlu benzoksazin polyesterlerinin sentezi ve termal özelliklerinin incelenmesi

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Abstract

In this study, benzoxazine-functionalized poly(ε-caprolactone) (BZ-PCL) was successfully synthesized, combining the advantageous properties of polybenzoxazines—such as easy synthesis comparable to phenolic resins, exceptional derivatization capabilities, environmentally friendly curing properties without releasing harmful byproducts, natural hydrophobicity, high mechanical strength, superior thermal stability, flame retardancy with low smoke emission, chemical resistance to solvents, acids and bases, and negligible volumetric shrinkage during curing—with the flexibility and processability of aliphatic polyesters. Initially, a dihydroxyl-functionalized benzoxazine monomer was synthesized. Subsequently, this dihydroxyl-functionalized benzoxazine monomer was incorporated into ε-caprolactone via ring-opening polymerization (ROP) in the presence of tin (II) 2-ethylhexanoate as a catalyst, yielding BZ-PCL. The number average molecular weight (M_n) of the benzoxazine-terminated polyester was found to be 39849 g/mol by gel permeation chromatography (GPC). The chemical structure of the dihydroxyl-functionalized benzoxazine monomer was confirmed by Proton Nuclear Magnetic Resonance (^{1}H NMR) and Fourier-transform infrared (FTIR) spectroscopy. The resulting BZ-PCL was comprehensively characterized using FTIR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TG). In this study, the obtained novel benzoxazine-functional poly(ε-caprolactone) exhibits different thermal properties than the poly(ε-caprolactone) homopolymer, demonstrating its potential as a high-performance polymer for advanced engineering applications.

Keywords: Di-benzoxazine, Poly(ε- caprolactone), Ring-opening polymerization

Öz

Bu çalışmada, polibenzoksazinlerin fenolik reçinelerle karşılaştırılabilir kolay sentezleri, olağanüstü türevlendirme yetenekleri, zararlı yan ürünler salmadan çevre dostu kürleme özellikleri, doğal hidrofobiklikleri, yüksek mekanik dayanımları, üstün termal kararlılıkları, düşük duman emisyonu ile alev geciktiricilikleri, çözücülere, asitlere ve bazlara karşı kimyasal dirençleri ve kürleme sırasında ihmal edilebilir hacimsel büzülmeleri gibi avantajlı özelliklerini alifatik polyesterlerin esnekliği ve işlenebilirliğiyle birleştiren, benzoksazin fonksiyonlu poli(ε-kaprolakton (BZ-PCL) başarıyla sentezlendi. Başlangıçta, dihidroksil fonksiyonlu bir benzoksazin monomeri sentezlendi. Daha sonra, bu dihidroksil fonksiyonlu benzoksazin monomeri, kalay (II) 2-etilheksanoat katalizörlüğünde halka açma polimerizasyonu yoluyla ε-kaprolaktona dahil edilerek BZ-PCL elde edildi. Benzoksazin uçlu poliesterin jel geçirgenlik kromatografisi (GPC) ile sayısal ortalama moleküler ağırlığı (M_n) 39849 g/mol olarak belirlendi. Dihidroksil fonksiyonlu benzoksazin monomerinin kimyasal yapısı Proton Nükleer Manyetik Rezonans (^{1}H NMR) ve Fourier dönüşümlü kızılötesi (FTIR) spektroskopisi ile doğrulandı. Elde edilen benzoksazin fonksiyonlu polikaprolakton, FTIR, diferansiyel tarama kalorimetrisi (DSC) ve termogravimetrik analiz (TGA) kullanılarak kapsamlı bir şekilde karakterize edildi. Bu çalışmada elde edilen yeni benzoksazin fonksiyonlu poli (ε-kaprolakton)un, poli (ε-kaprolakton) homopolimerinden farklı termal özellikler göstermesi, ileri mühendislik uygulamaları için yüksek performanslı bir polimer potansiyelini de göstermektedir.

Anahtar kelimeler: Di-benzoksazin, Poli (ε-kaprolakton), Halka açma polimerizasyonu

1 Introduction

Polybenzoxazines [1–4] are heat-curable phenolic resins that have gained considerable interest due to their superior thermal stability, inherent flame retardancy, low water absorption, chemical resistance, and excellent dimensional stability. These properties make them suitable for a wide range of applications, particularly in high-performance fields such as aerospace and advanced composites. Polybenzoxazines are generally formed through thermally induced ring-opening polymerization (ROP) of benzoxazine monomers [5] without the need for catalysts or the generation of volatile byproducts. Although cationic initiators have also been reported to promote polymerization [6]. In some benzoxazines, ring opening has been observed

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Geliş / Received: 27.03.2026 Kabul / Accepted: 27.07.2026 Yayımlanma / Published: 24.08.2026
doi: 10.28948/ngumuh.1916858

in the presence of compounds with active hydrogen (HY), such as naphthol, indoles, carbazoles, imides, aliphatic nitro compounds, and even phenol, resulting in the formation of small oligomers as byproducts [7]. Benzoxazine monomers are readily synthesized via Mannich-type reactions of phenols, formaldehyde, and primary amines, allowing structural flexibility and the incorporation of functional groups such as acetylene, nitrile, propargyl, and maleimide moieties to tailor material properties [8–12].

The integration of benzoxazine groups into polymer units is recognized as a highly effective and advanced approach for structural modification of polymers. The incorporation of benzoxazine functionalities into polymer architecture has garnered considerable attention in recent years, owing to the superior thermal, mechanical, and chemical properties of benzoxazine-based network structures. A significant benefit of these systems is their high thermal stability. The high aromatic rigid structure and cross-linking density contribute to an increase in the glass transition temperature of the amorphous or semi-crystalline polymer, and to an improvement in its thermal degradation resistance. Indeed, the extant literature attests to the synthesis of phenyl phosphine oxide-based polymers, with concomitant significant enhancement of their thermal properties, consequent to the incorporation of benzoxazine monomer within the polymer structure [13]. Despite the numerous advantages traditionally attributed to phenolic polymers, including flame retardancy, inherent hardness, dielectric insulation properties, and high temperature resistance, their brittleness, the necessity for strong acid catalysts, short shelf life, and, most significantly, the absence of structural design flexibility [14] render them inferior to benzoxazine-modified polymers. The hydrophobic ring structure of aromatic benzoxazine allows for the preservation of mechanical and electrical properties in humid environments. Furthermore, the network structures formed by heat curing of benzoxazine provide high resistance to chemicals and corrosion, extending the service life of materials under harsh conditions [15]. In a similar way, the incorporation of benzoxazine groups into polymer systems endows the material with inherent flame-retardant properties [16]. During the thermal decomposition of the polymeric material, the char yield of phenolic compounds is high, thus significantly reducing flame propagation. This makes the use of halogen-based flame retardants redundant, thus providing an environmentally friendly and sustainable solution. This property is significant, particularly in the domains of electronic and structural materials applications, as well as aerospace applications [17-19]. It is evident that benzoxazines exhibit a high degree of susceptibility to structural functionalization. The integration of benzoxazine functionalities into polymer systems [20] can be achieved through the selection of phenolic and amine precursors, resulting in linear, branched, or cross-linked polymer structures. The incorporation of benzoxazine groups into polymer main chains can occur in two distinct configurations: either side chains or pendulums. This allows for the modification of different polymer matrices such as polycaprolactone (PCL), polyethylene glycol, epoxy, and polyurethane [21,22]. Furthermore, it has been demonstrated that the hydroxyl groups released during the curing of benzoxazine in polymer composites enhance interfacial interaction by increasing secondary interactions with reinforcing fibres, inorganic salts, and inorganic metal oxides. This has been demonstrated to enhance load transfer efficiency in composite systems and adhesion to different substrates in coating applications. As a result, the integration of benzoxazine groups into polymer systems offers a powerful strategy that simultaneously improves fundamental properties such as thermal stability, moisture resistance, flame retardancy, and structural flexibility [23-25]. Hatsuo Ishida and Y. H. Lee reported that polybenzoxazine/PCL blends exhibited synergistic improvements in thermal stability and viscoelastic behavior, indicating strong intermolecular interactions between the benzoxazine network and PCL chains [26]. Similarly, Sunan Tiptipakorn, Naritsara Chaipakdee, Sarawut Rimdusit, Kasinee Hemvichian, and Pattra Lertsarawut demonstrated that the molecular weight of PCL significantly affects the mechanical properties, thermal behavior, and shape memory performance of bio-based polybenzoxazine/PCL blends [27]. While the literature mostly examines polybenzoxazine/PCL blend systems, this study is significant because it directly synthesizes a benzoxazine-functionalized PCL structure and investigates its thermal behavior.

In this study, benzoxazine-functionalized poly(ε-caprolactone) (BZ-PCL) was successfully synthesized due to its superior properties mentioned above. For this purpose, firstly, a dihydroxyl-functionalized benzoxazine monomer was synthesized. Then, it was incorporated into poly(ε-caprolactone) by ROP. The structural and thermal properties of the resulting polymer were investigated. Consequently, benzoxazine functional polymers are hypothesized to be promising materials for advanced engineering applications.

2 Materials and methods

2.1 Material

Bisphenol-A (4-[1-(4-hydroxyphenyl)-1-methylethyl] phenol, Catalog No: 239658-50G, 99+%) and ε-caprolactone (2-oxepanone, CAS No: 502-44-3, 99%) were purchased from Merck (Darmstadt, Germany). Paraformaldehyde ($(CH_2O)_n$, CAS No: 30525-89-4, 98%), ethanolamine (2-aminoethanol, CAS No: 141-43-5, 99%), ethanol (ethyl alcohol, CAS No: 64-17-5, 99+%), dichloromethane (methylene chloride, CAS No: 75-09-2, 99.8%), sodium chloride (NaCl, CAS No: 7647-14-5, 99%), sodium hydroxide (caustic soda, CAS No: 1310-73-2, 99%), magnesium sulfate ($MgSO_4$, CAS No: 10034-99-8, 99%), and *N, N*-dimethylformamide (DMF, CAS No: 68-12-2, 99.8%) were also obtained from Merck (Darmstadt, Germany). Tin (II) 2-ethylhexanoate (2-ethylhexanoic acid tin (II) salt, CAS No: 301-10-0, 98%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals were of analytical grade and used as received without further purification. Conventional Schlenk tube techniques were employed for all reactions.

2.2 Characterization techniques

Fourier-transform infrared spectroscopy (FTIR) analyses were performed using a PerkinElmer Spectrum Two FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) accessory. Proton Nuclear Magnetic Resonance (^{1}H NMR) (400 MHz) spectra were obtained on a Varian AS-400 spectrometer using $CDCl_3$ as the solvent and tetramethyl silane (TMS) as the internal reference. Chemical shift values are expressed in parts per million (ppm), and coupling constants (J) are reported in hertz (Hz). Thermal properties of BZ-PCL were investigated by thermogravimetric analysis (TG) using a PerkinElmer Pyris 1 instrument over a temperature range of 25–800°C at heating rates of 20 °C/min under a nitrogen atmosphere. The experiment was conducted using a PerkinElmer Diamond DSC, a sophisticated instrument that employs differential scanning calorimetry (DSC) to analyze the thermal behavior of PCL over a temperature range of 25–350 °C at heating rates of 10 °C/min under a nitrogen atmosphere. Number-average (M_n) and weight-average (Mw) molecular weights of the synthesized polymer with hydroxyl function were determined by gel permeation chromatography (GPC) using differential refractive index detectors. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL/min, and molecular weight distributions and polydispersity indices were calculated relative to monodisperse polystyrene standards.

2.3 Synthesis of dihydroxyl-functionalized benzoxazine

Dihydroxyl-functionalized benzoxazine monomer was synthesized (Figure 1) according to a literature-reported procedure [28,29]. Paraformaldehyde (1.51 g, 0.05 mol) and bisphenol A (2.94 g, 0.0125 mol) were charged into a two-necked round-bottom flask, followed by the addition of ethanolamine (1.53 g, 0.025 mol) and ethanol as the solvent. The reaction mixture was refluxed at 79 °C under continuous magnetic stirring for 24 h. After completion of the reaction, ethanol was removed under reduced pressure using a rotary evaporator. The residue was dissolved in approximately 50 mL of dichloromethane and transferred to a separatory funnel. The organic phase was washed once with 0.1 N NaOH solution (0.005 mol) and three times with 0.1 N NaCl solution (0.005 mol). The organic layer was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure to afford the dihydroxyl-functional benzoxazine monomer. The reaction yield was calculated to be 63% (open yellow). The dihydroxyl-functional benzoxazine was characterized by using FTIR, ^{1}H NMR, GPC, and TG/DTG methods.

2.4 Synthesis of dihydroxyl-functionalized benzoxazine poly(ε-caprolactone)

The synthesis of BZ-PCL was conducted via ROP of ε-caprolactone, utilizing a dihydroxyl-functionalized benzoxazine monomer and tin (II) 2-ethylhexanoate [$Sn(Oct)_2$] as a catalyst. For this purpose, ε-caprolactone (1.13 g, 0.01 mol) and dihydroxyl- functionalized benzoxazine monomer (0.41 g, 0.001 mol)

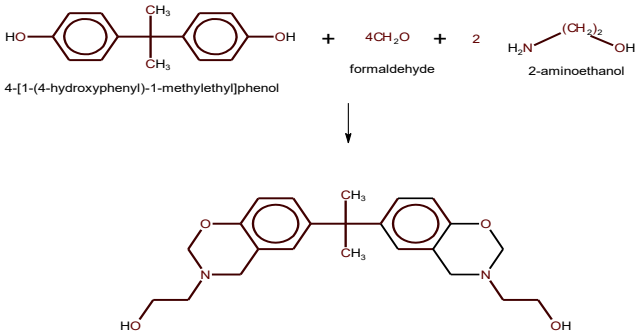


Figure 1. Synthesis of dihydroxyl-functionalized benzoxazine

were placed in a two-necked round-bottom flask under a nitrogen atmosphere. Subsequently, [$Sn(Oct)_2$] (Tin (II) 2-ethylhexanoate) was introduced as a catalyst at a concentration of 0.1 mol % (2.5×10^{-6} mol) with respect to the quantity of caprolactone. To establish an inert atmosphere, the process of vacuum-nitrogen cycling was employed to remove oxygen and moisture from the system. The system was heated to 110 °C under a nitrogen atmosphere with magnetic stirring, and polymerization continued at this temperature for 24 h. The resulting polymer was dissolved in dichloromethane and precipitated into cold methanol. The precipitated polymer was isolated from the dichloromethane by decantation and subsequently dried in a vacuum oven for a period of 6 h. This process yielded 0.25 g of BZ-PCL. The reaction yield was found to be 61% (white). The synthesis reaction is shown in Figure 2. The molecular weight of BZ-PCL was found to be 39849 g/mol.

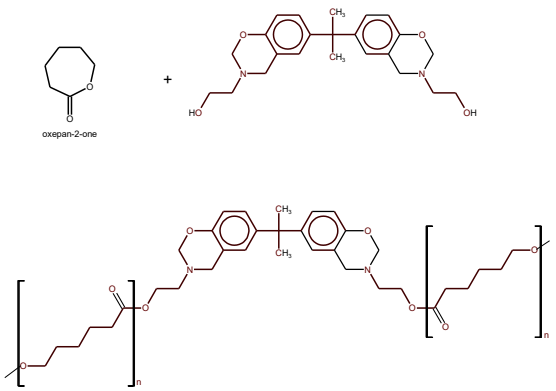


Figure 2. Synthesis of BZ-PCL

The moderate yields obtained for the hydroxyl-functionalized benzoxazine monomer (63%) and benzoxazine-functionalized BZ-PCL (61%) may be attributed to purification losses during precipitation and washing processes, as well as possible side reactions such as partial self-polymerization of benzoxazine groups and transesterification during ROP.

2.5 Solubility tests of BZ-PCL in different solvents

Solubility tests in different solvents were performed to reveal the chain length and consequently the molecular weight, the network-like cross-linking status, the percentage

of amorphous and crystalline structures, the degree of functionality of the side groups attached to the main chain, and the chemical structure of polymers. These tests can generally be used to characterize the macromolecule obtained after polymer synthesis, determine its processability, and identify various application areas. Table 1 shows the solubility of Benzoxazine-functionalized poly(ε-caprolactone) in various solvents.

2.6 Thermal Properties of Benzoxazine Functionalized PCL

DSC and TG analyses were used to determine the thermal properties, heat-sensitive behavior, and application areas of benzoxazine-functionalized PCL. Thermal properties of BZ-PCL were determined using a PerkinElmer Pyris 1 and PerkinElmer Diamond DSC devices.

3 Results and discussion

3.1 FTIR analysis

The FTIR spectrum of the dihydroxyl-functionalized benzoxazine monomer is presented in Figure 3**.** A broad absorption band centered at approximately 3399 cm^{-1} is assigned to the stretching vibration of hydroxyl –OH groups originating from the dihydroxyl-functionalized benzoxazine structure. The absorption bands observed at 2998 cm^{-1} and 2950 cm^{-1} are attributed to the aliphatic C–H stretching vibrations of the methylene groups present in the benzoxazine structure. The characteristic band at 1612 cm^{-1} corresponds to the aromatic C=C stretching vibration. Furthermore, the absorption peak at 1253 cm^{-1} is assigned to the C–N stretching vibration of the oxazine ring, while the bands at 1181 cm^{-1} and 1111 cm^{-1} are attributed to the C–C and C–O–C stretching vibrations, respectively. These characteristic absorption bands are in good agreement with the FTIR spectrum of hydroxyl-functionalized benzoxazine monomers reported in the literature [30].

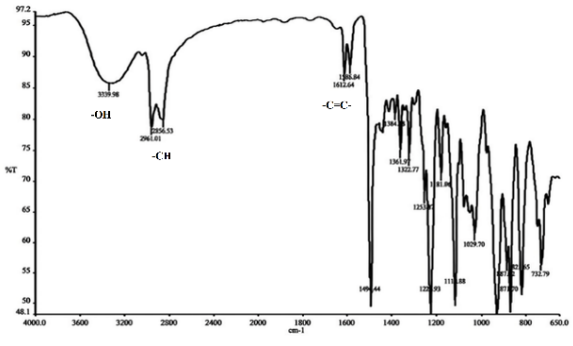


Figure 3. FTIR spectrum of dihydroxyl-functionalized benzoxazine

The FTIR spectrum of the BZ-PCL is shown in Figure 4. The absorption bands at 2919 cm^{-1} and 2851 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of aliphatic C–H groups in the PCL backbone. A strong absorption band appearing at 1728 cm^{-1} is attributed to the ester carbonyl C=O stretching vibration, which is the characteristic absorption band of the PCL structure. In addition, the bands observed at 1259 cm^{-1}, 1232 cm^{-1}, 1158 cm^{-1}, and 1091 cm^{-1} correspond to the C–O and C–O–C stretching vibrations of the polyester backbone. The aromatic C=C stretching vibration around 1611 cm^{-1}, together with the C–N–C/C–N vibrations in the 1200–1300 cm^{-1} region, confirms that the benzoxazine moieties remain attached to the polymer chain after polymerization.

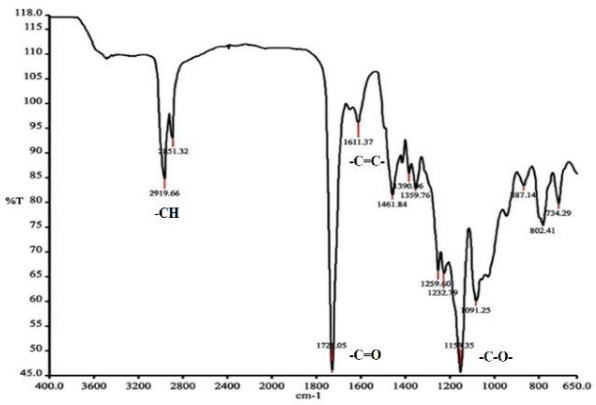


Figure 4. FTIR spectrum of BZ-PCL

Compared with the spectrum of the dihydroxyl-functionalized benzoxazine monomer, the broad hydroxyl –OH absorption band observed around 3399 cm^{-1} disappears (or is significantly reduced) after ROP, while a new strong ester carbonyl band appears at 1728 cm^{-1}. These spectral changes clearly demonstrate that the hydroxyl-functionalized benzoxazine successfully initiated the ROP of ε-caprolactone, leading to the formation of benzoxazine-functionalized poly(ε-caprolactone). Therefore, the FTIR results provide strong evidence for the successful synthesis of the target polymer.

3.2 ^{1}H NMR analysis

The ^{1}H NMR spectrum [31] of dihydroxyl functional benzoxazine can be seen in Figure 5. In the ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, the signal at δ 1.59 ppm (d, 3H, J = 6.8 Hz) was assigned to the methyl ($–CH_3$) protons attached to the carbon adjacent to nitrogen. The signals observed at δ 2.94–3.04 ppm (q, 2H) correspond to the methylene ($–CH_2–$) protons attached to nitrogen. The peaks at δ 3.65–3.96 ppm were attributed to the methylene protons adjacent to the hydroxyl group ($–CH_2OH$). The characteristic oxazine ring methylene protons located between nitrogen and oxygen/aromatic ring appeared at δ 4.81–5.91 ppm. In addition, the signals in the aromatic region at δ 6.66–7.08 ppm were assigned to aromatic protons of the benzene ring. These results confirm the successful formation of the dihydroxyl-functionalized benzoxazine monomer.

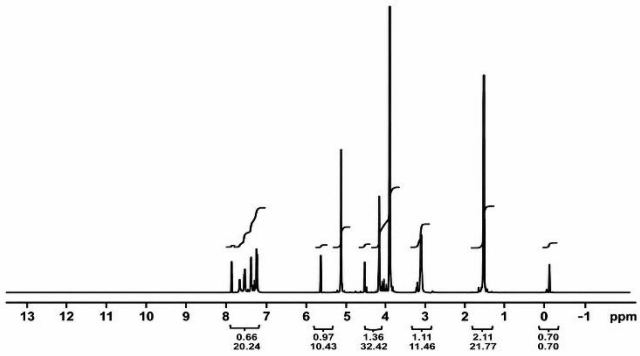


Figure 5. ^{1}H NMR spectrum of dihydroxyl-functionalized benzoxazine

Table 1. Solubility tests of benzoxazine-functionalized poly(ε-caprolactone) in different solvents

Solvents	Solubility at Room Temperature	Solubility When Heated
Methanol	---	■
Ethanol	---	---
Acetone	---	■
Water	---	---
Hexane	---	---
Dichloromethane	---	■
Chloroform	■	■
Dimethyl sulfoxide	---	---
Dimethylformamide	---	---
Diethyl ether	■	■
Tetrahydrofuran	---	---

3.3 Thermal analysis

The thermal characteristics of the benzoxazine-functionalised poly(ε-caprolactone) were investigated by TG analysis. The thermogram is presented in Figure 6. The TG/DTG results demonstrate distinct thermal degradation behaviors for neat PCL and BZ-PCL. Pure PCL exhibited a single-step degradation profile with a rapid weight loss occurring between approximately 350 and 360 °C, indicating the typical thermal decomposition behavior of the aliphatic polyester backbone. After the main degradation step, only a very small char residue remained at higher temperatures, confirming the limited thermal stability of neat PCL.

In contrast, the BZ-PCL showed a broader and more gradual degradation process. The onset of degradation occurred at slightly lower temperatures due to the decomposition of benzoxazine-related functional groups; however, the material retained significantly higher residual weight at elevated temperatures. The enhanced char formation observed above 500 °C suggests the development of a thermally stable aromatic network structure originating from the benzoxazine moieties.

Furthermore, the higher residual mass of BZ-PCL compared to neat PCL indicates improved thermal resistance and carbonization ability. This behavior can be attributed to the crosslinked aromatic structures formed during thermal decomposition, which suppress volatilization and promote char formation. Overall, the incorporation of benzoxazine functionalities enhanced the thermal stability and high-temperature durability of PCL.

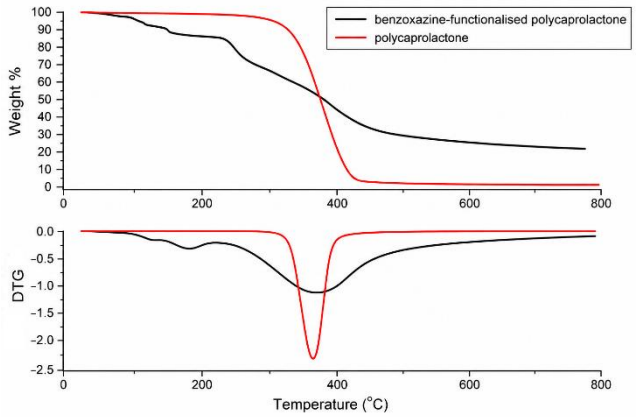


Figure 6. TG curves of PCL and BZ-PCL

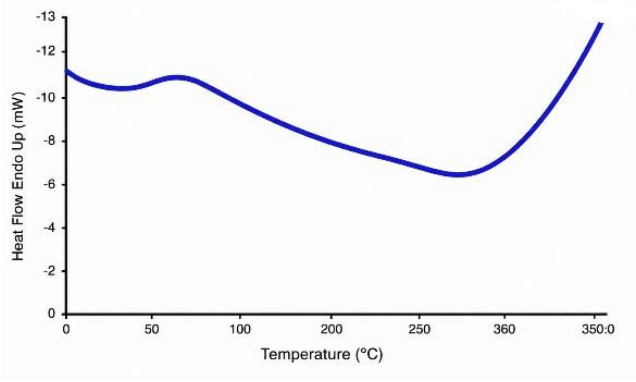


Figure 7. DSC curves of BZ-PCL

The analysis of the DSC curve (Figure 7) showed that the weak endothermic activity observed at low temperatures is consistent with the initial mass loss and is related to the removal of moisture and volatile components. The intense heat flow variations observed at higher temperatures were consistent with the degradation step of the polymer main chain observed in TG, confirming that the degradation at these temperatures is exothermic. Considering these results, it was clearly seen that BZ-PCL is thermally stable up to approximately 250 °C, but the structural degradation of poly(ε-caprolactone) accelerates at higher temperatures.

4 Conclusion

In this study, BZ-PCL was successfully synthesized via ROP using a dihydroxyl-functionalized benzoxazine monomer. First of all, a dihydroxyl-functionalized benzoxazine monomer was synthesized. Subsequently, this dihydroxyl-functionalized benzoxazine monomer was incorporated into ε-caprolactone via ROP in the presence of tin (II) 2-ethylhexanoate as a catalyst, yielding BZ-PCL. The number-average molecular weight of the benzoxazine-terminated polyester was found to be 39849 g/mol by GPC. Structural and thermal characterizations by FTIR, ^{1}H NMR, DSC, and TG confirmed the successful incorporation of

benzoxazine functionalities into the PCL backbone. Benzoxazine-functionalized poly(ε-caprolactone) was observed to dissolve best in chloroform and diethyl ether solvents, respectively, at room temperature. According to the TG results, the maximum decomposition temperature of BZ-PCL was found to be around 357 °C. The synthesized material combines the advantageous properties of polybenzoxazines, including high thermal and mechanical stability, flame resistance, chemical resistance, and minimal volumetric change upon curing. The novel BZ-PCL obtained in this study exhibits different thermal properties than PCL homopolymer, demonstrating its potential as a high-performance polymer for advanced engineering applications.

CRediT authorship contribution statement

Berna Körpınar: Data organization, Methodology, Software, Visualization, Writing, Review, and Editing

Conflict of interest

The author declare that there is no conflict of interest.

Similarity rate (iThenticate): 19%

Declaration of generative artificial intelligence (AI) and AI-assisted technologies in the writing process

During the preparation of this manuscript, ChatGPT (Open AI) was used solely to improve the language and readability of the manuscript. The AI tool was not used to generate scientific content, interpret results, draw conclusions, or make scientific decisions. After using this tool, the author critically reviewed, revised, and edited all content as necessary and takes full responsibility for the accuracy, originality, and integrity of the final manuscript.

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