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Structure-property correlations in aromatic polyesters: A Comparative TGA and DSC study of naphthyl-benzamide derivatives

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Abstract

Aromatic polyesters are valued for their thermal stability, chemical resistance, and mechanical strength, but poor solubility and high glass transition temperatures (Tg) limit their processability. To address this, two novel diols, 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide (XV, 1-naphthyl) and 3,5-dihydroxy-N-(4-(naphthalen-7-yloxy)phenyl)benzamide (XVIII, 2-naphthyl), were synthesized and polymerized with isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) via interfacial polycondensation.

The resulting polyesters were characterized by FTIR and NMR, and their thermal properties were studied using TGA and DSC. All polymers showed decomposition onset above 150 °C with T10 values of 355-467 °C. The XVIII series exhibited higher char yields and Tg values (129-147 °C) compared to the XV series (109-129 °C), indicating greater rigidity and thermal resistance.

These results highlight the critical role of pendant group orientation in controlling thermal stability and chain mobility, offering design strategies for advanced high-performance polyesters.

Keywords: TGA, DSC, aromatic polyesters, naphthyl-benzamide, thermal stability

1. Introduction

Aromatic polyesters represent one of the most important families of high-performance polymers because of their unique combination of desirable physical, chemical, and thermal properties. Their backbones, composed primarily of aromatic rings and ester linkages, provide high rigidity, excellent resistance to solvents and chemicals, and superior mechanical durability. These features make them highly attractive for use in advanced engineering and industrial applications, including electronic packaging, aerospace components, protective coatings, high-strength fibers, and biomedical devices. The presence of aromatic units in the backbone confers high stability, while the ester functionalities contribute to thermal robustness, rendering these polymers capable of performing in demanding environments [1-18]. Despite these advantages, conventional aromatic polyesters suffer from some significant limitations. Their rigid backbone structure and strong intermolecular interactions, primarily through π-π stacking and hydrogen bonding, lead to poor solubility in common organic solvents. This, in turn, results in high glass transition temperatures (Tg) and poor melt processability, which restrict their wider adoption in applications where ease of processing is critical. Therefore, the challenge for polymer chemists lies in designing and synthesizing new aromatic polyester systems that retain the excellent thermal and mechanical characteristics of the traditional ones while simultaneously overcoming the drawbacks of poor solubility and high rigidity [19-32].

A variety of strategies have been investigated to address these challenges. One widely used approach involves the incorporation of flexible ether linkages into the polymer backbone, which reduces chain rigidity and lowers the Tg. Similarly, the introduction of non-coplanar or cardo groups, such as fluorene, phthalimidine, and cyclohexyl units, has been shown to disrupt chain packing and improve solubility while maintaining thermal stability. Asymmetric structures and bulky pendant moieties have also been successfully incorporated into aromatic polyesters to generate free volume, weaken intermolecular forces, and reduce chain packing density. Collectively, these modifications provide opportunities to tailor the balance between processability and stability [33-38].

Among these structural modifications, the introduction of pendant aromatic substituents has attracted particular attention. Pendant groups can significantly alter the spatial arrangement of polymer chains, leading to pronounced changes in solubility, flexibility, and thermal behavior. In particular, naphthyl-based pendant groups are especially promising because of their extended aromatic nature, which can both enhance chain rigidity and influence intermolecular interactions. Furthermore, the orientation of the naphthyl group whether attached through the 1-position or the 2-position can result in distinct differences in polymer chain packing and macroscopic properties [39-41].

The present work focuses on a comparative investigation of two novel aromatic polyesters derived from structurally related diols that differ only in the orientation of the pendant naphthyl-benzamide group. The first diol, 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide (XV), is based on 1-naphthol, while the second diol, 3,5-dihydroxy-N-(4-(naphthalen-7-yloxy)phenyl)benzamide (XVIII), is based on 2-naphthol. Both diols were synthesized through aromatic nucleophilic substitution, reduction, and Yamazaki phosphorylation reactions, and then polymerized with isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) using an interfacial polycondensation technique.

The synthesized polyesters were characterized using Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy to confirm their chemical structures. Their thermal behavior was systematically examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in order to understand the influence of pendant group orientation on decomposition profiles, char yield, and glass transition temperatures. By comparing the thermal properties of the XV-based and XVIII-based series, this work aims to establish structure-property correlations that can guide the rational design of next-generation aromatic polyesters with balanced thermal stability, rigidity, and processability.

2. Experimental

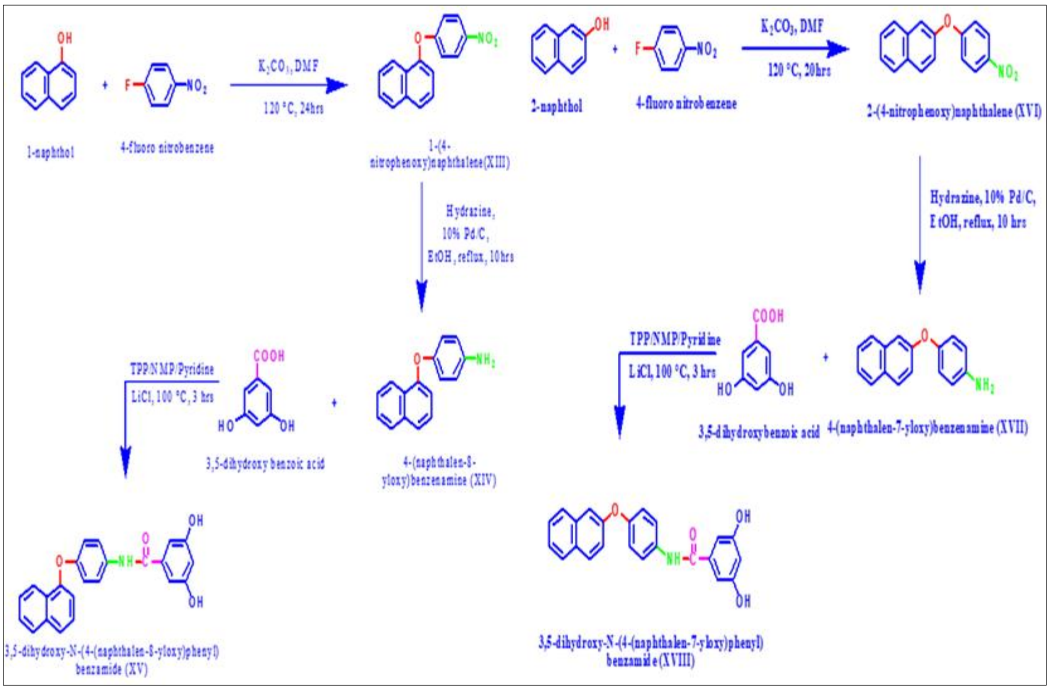
2.1 Materials: All reagents and solvents used in this study were of analytical grade and were employed as received unless otherwise specified. 1-Naphthol and 2-naphthol were used as starting materials for the preparation of diols XV and XVIII, respectively. 4-Fluoronitrobenzene was selected as the electrophilic aromatic substitution partner. Anhydrous potassium carbonate served as a base during the nucleophilic substitution reactions, while hydrazine hydrate in the presence of palladium on activated carbon (10%) was employed as the reducing agent for the conversion of nitro intermediates to the corresponding amines.

Dimethylformamide (DMF) was used as a high-boiling polar aprotic solvent for substitution reactions, and ethanol and methanol were used in crystallization and recrystallization steps. Lithium chloride, pyridine, and N-methyl-2-pyrrolidone (NMP) were employed in the Yamazaki phosphorylation reaction for the synthesis of diols. Triphenyl phosphate was used as the condensing agent. For polymerization, isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) were used as diacid chlorides, while benzyl triethyl ammonium chloride (BTEAC) served as the phase-transfer catalyst. All solvents, including dichloromethane and hexane, were of reagent grade. Distilled water was used for aqueous reaction phases and for washing the crude products.

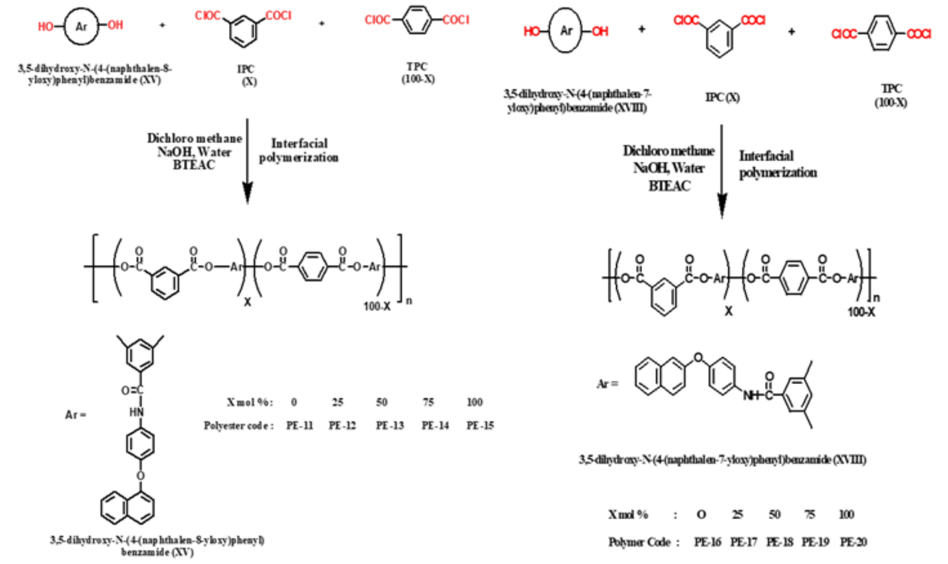
2.2 Synthesis of Diols and Polyesters

The two diols, 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide (XV) and 3,5-dihydroxy-N-(4-(naphthalen-7-yloxy)phenyl)benzamide (XVIII), were synthesized through a three-step process consisting of aromatic nucleophilic substitution, catalytic reduction, and condensation via Yamazaki phosphorylation.

In the first step, either 1-naphthol or 2-naphthol was reacted with 4-fluoronitrobenzene in DMF in the presence of anhydrous potassium carbonate at 120 °C for 20 h to afford the nitro-substituted intermediates. These intermediates were then subjected to catalytic reduction using hydrazine hydrate in ethanol with palladium on activated carbon (10%) as the catalyst, yielding the corresponding amine precursors.



Scheme 1: Synthesis of Diol Monomers



Scheme 2: Synthesis of Polyesters

In the final step, the amines were condensed with 3,5-dihydroxybenzoic acid in the presence of lithium chloride, pyridine, and triphenyl phosphate in NMP to give the target diols XV and XVIII. As shown in scheme 1. The crude products were purified by recrystallization from ethanol, and their structures were confirmed by FTIR and ^1H NMR spectroscopy, as shown in Figure 1-4.

The synthesized diols were subsequently polymerized with IPC and TPC by interfacial polycondensation. Aqueous sodium hydroxide was used to dissolve the diol monomer, and benzyl triethyl ammonium chloride was employed as a phase-transfer catalyst. A dichloromethane solution of IPC and/or TPC was added dropwise to the aqueous diol solution with vigorous stirring at 30 °C. After 1 h of reaction, the viscous solution was poured into excess hexane to precipitate the polyester. The resulting polymers were collected by filtration, thoroughly washed with water, and dried under vacuum at 80 °C for 10 h. As shown in scheme 2. All polyesters were obtained in yields greater than 90%.

Spectroscopic Characterization

The chemical structures of the synthesized diols XV and XVIII were confirmed by FTIR, ^{1}H NMR

- FTIR: Figure 1 Diol XV showed characteristic absorptions at 3300 cm^{-1} (-OH), 2970 cm^{-1} (-NH), and 1648 cm^{-1} (C=O).
- FTIR: Figure 2 Diol XVIII exhibited similar bands at 3311 cm^{-1} (-OH), 2968 cm^{-1} (-NH), and 1660 cm^{-1} (C=O).
- ^{1}H NMR Figure 3 (Diol XV) (DMSO, 400MHz) δ (ppm): 6.3 (S, 1H), 6.7 (S, 2H), 6.8 (d, 1H), 6.9 (d. 2H), 7.3 (d, 1H), 7.4 (dd, 1H), 7.5 (dd, 1H), 7.7 (d, 2H), 7.8 (dd, 1H), 7.9 (d, 1H), 8.1 (d, 1H).
- ^{1}H NMR Figure 4 (Diol XVIII) (DMSO, 400MHz) δ (ppm): 6.3 (S, 1H), 6.7 (d, 2H), 7.0 (d, 2H), 7.2 (s. 1H), 7.3 (d, 1H), 7.4 (dd, 2H), 7.68 (d, 1H), 7.8 (d, 4H), 9.4 (s, 2H), 10.05(s, 1H).

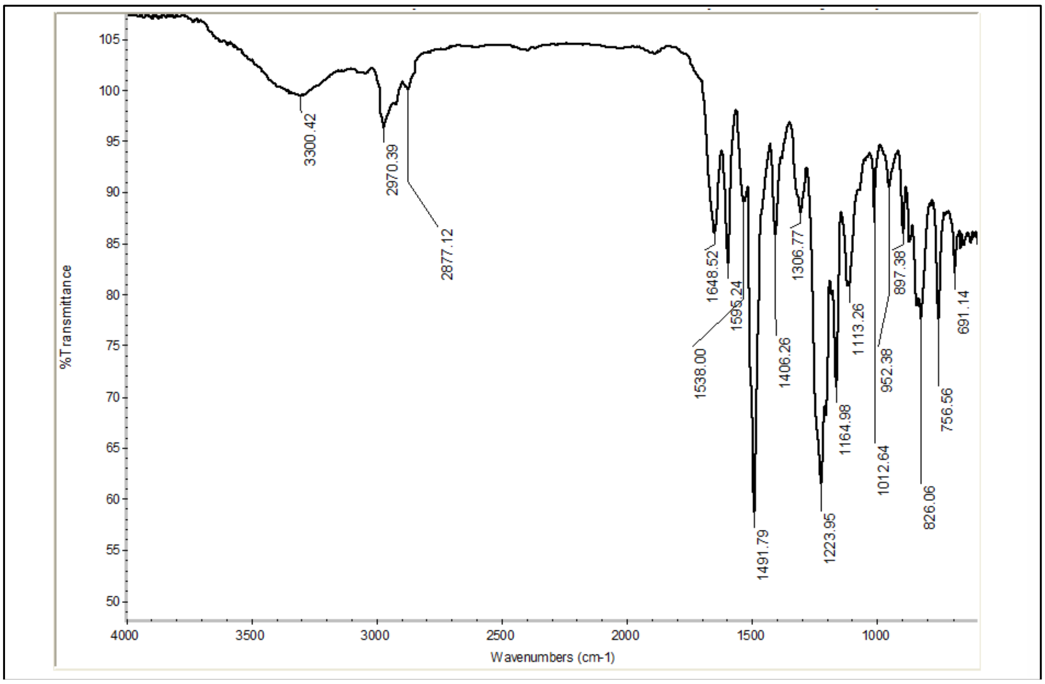


Fig 1: FT-IR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide (XV)

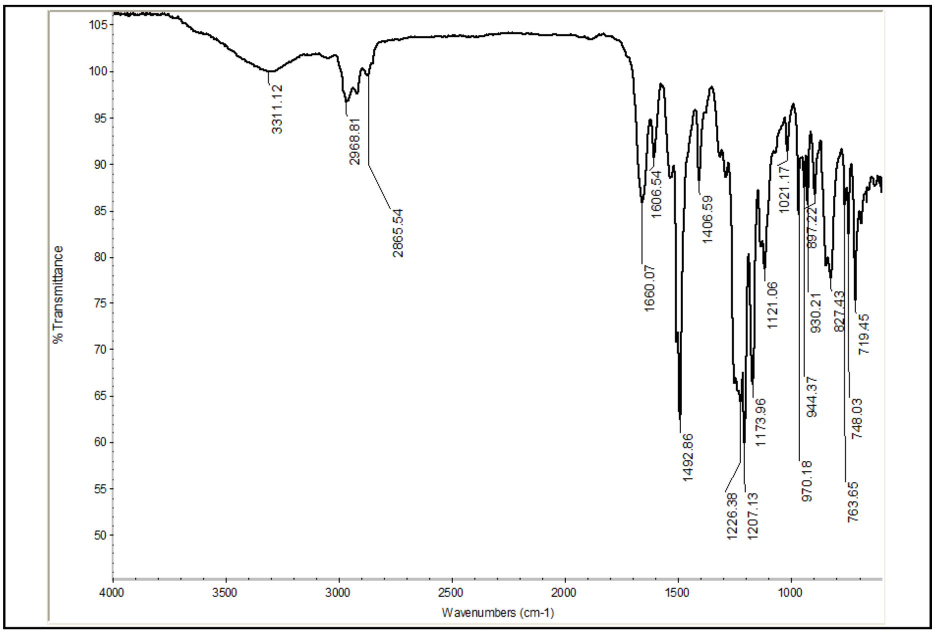


Fig 2: FT-IR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-7-yloxy)phenyl)benzamide (XVIII)

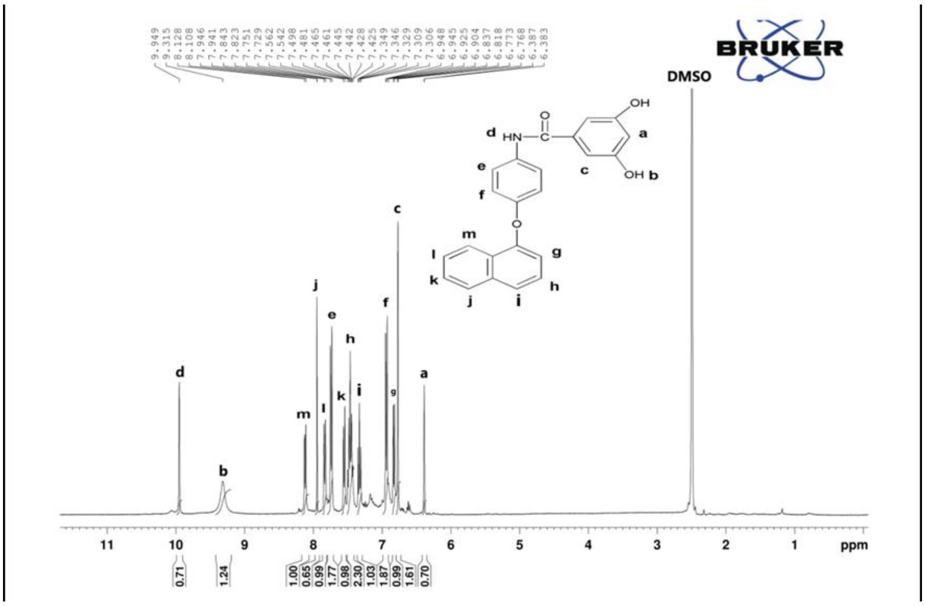


Fig 3: ^{1}H NMR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide (XV)

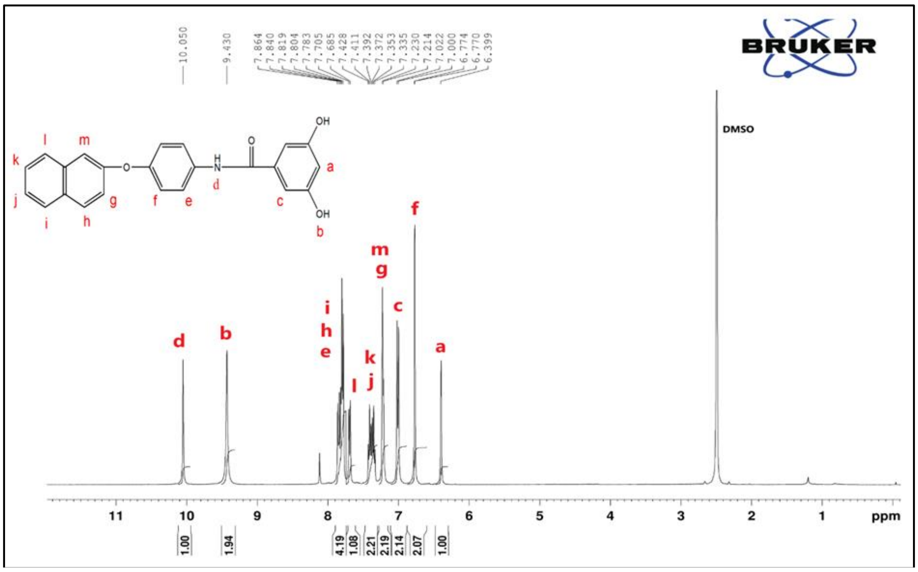


Fig 4: ^{1}H NMR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-7-yloxy)phenyl)benzamide (XVIII)

3. Results and Discussion

3.1 Thermogravimetric Analysis (TGA)

The thermal degradation behavior of the synthesized polyesters was examined by thermogravimetric analysis (TGA) under a nitrogen atmosphere, and the results are summarized for both the XV- and XVIII-derived series. The XV-based polyesters, prepared from the 1-naphthyl diol (XV), exhibited initial decomposition temperatures (Ti) in the range of 151-169 °C, indicating that the onset of degradation begins at moderately high temperatures. The temperature corresponding to 10% weight loss (T10) was found to lie between 369 and 425 °C for this series. The char yields at 800 °C ranged from 30% to 44%, reflecting the stability of the aromatic framework and the ability of the polymer to form a stable carbonaceous residue after volatilization of labile components. The results are presented in Figure 3 and 4.

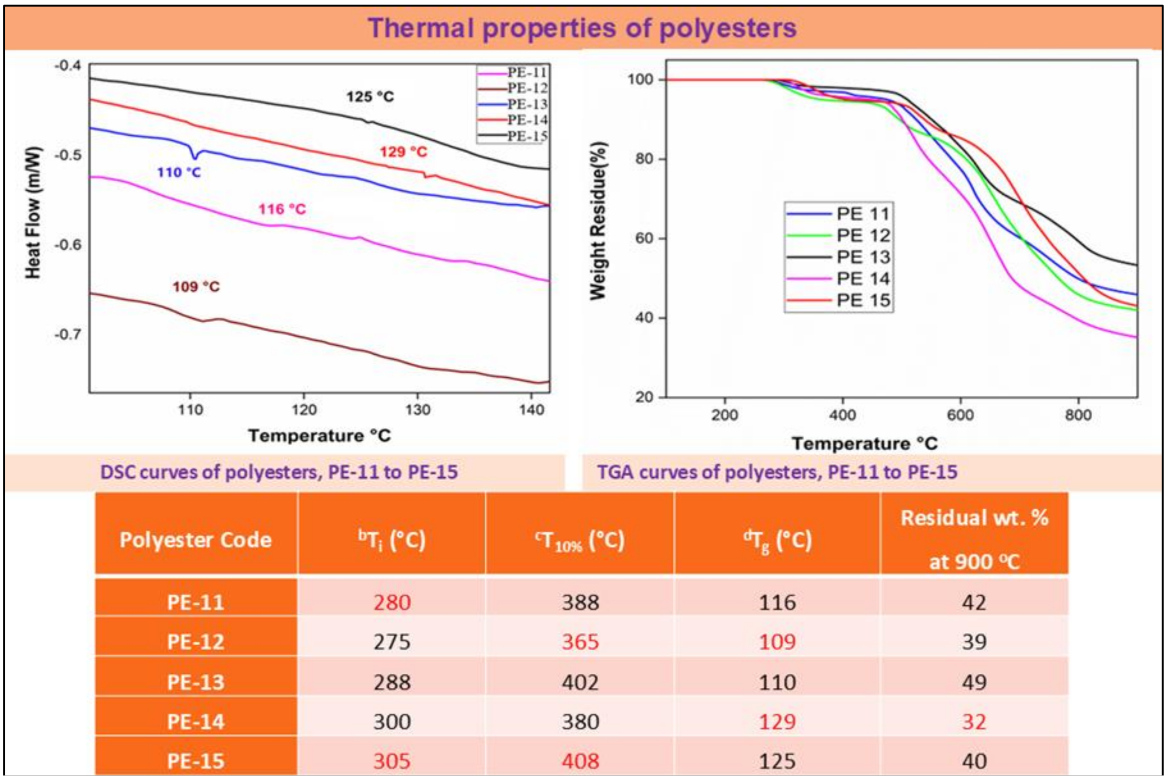
In comparison, the XVIII-based polyesters, derived from the 2-naphthyl diol (XVIII), showed a slightly narrower range of Ti values, between 151 and 164 °C. Although the initial decomposition temperatures were comparable to those of the XV series, a clear distinction was observed in the T10 values. For the XVIII polyesters, the T10 extended over a wider range, from 355 to as high as 467 °C. This suggests that while the onset of decomposition occurred at similar temperatures, the resistance to progressive weight loss was greater in the XVIII series. The char yields at 800 °C were slightly higher as well, ranging from 36% to 44%. This behavior indicates improved thermal resistance, which can be attributed to the more compact and efficient chain packing facilitated by the orientation of the pendant 2-naphthyl group. The stronger intermolecular interactions and reduced free volume in these polymers limit the mobility of chain segments and enhance their ability to withstand high temperatures before decomposition.

These results clearly demonstrate that the subtle difference in pendant orientation has a measurable impact on the degradation pathway and residue stability of the resulting polyesters. The XVIII-based materials are thermally more robust, which is advantageous for high-temperature applications.

3.2 Differential Scanning Calorimetry (DSC)

The glass transition temperatures (Tg) of the polyesters were determined by DSC to provide insights into chain mobility and the rigidity of the polymer backbone. The XV-based series exhibited Tg values in the range of 109-129 °C. These relatively lower Tg values reflect greater flexibility within the polymer chains, which arises from the orientation of the pendant 1-naphthyl group. The 1-naphthyl orientation introduces steric hindrance that disrupts regular chain packing, thereby generating additional free volume and reducing the energy required for cooperative segmental motion of the chains. The results are presented in Figure 3 and 4.

By contrast, the XVIII-based polyesters consistently displayed higher Tg values, ranging from 129 to 147 °C. The elevated Tg values can be explained by the more linear orientation of the pendant 2-naphthyl groups, which facilitates closer chain packing and enhances intermolecular interactions. This compact packing restricts chain segment mobility and requires a higher thermal input to achieve the onset of the glass transition. As a result, the XVIII series can be considered more rigid and thermally resistant compared to their XV counterparts. The comparison of Tg values between the two series highlights the strong influence of pendant orientation on chain dynamics. The shift of nearly 20 °C in Tg between the XV and XVIII polyesters illustrates how even minor structural modifications in pendant position can significantly alter macroscopic thermal behaviour.

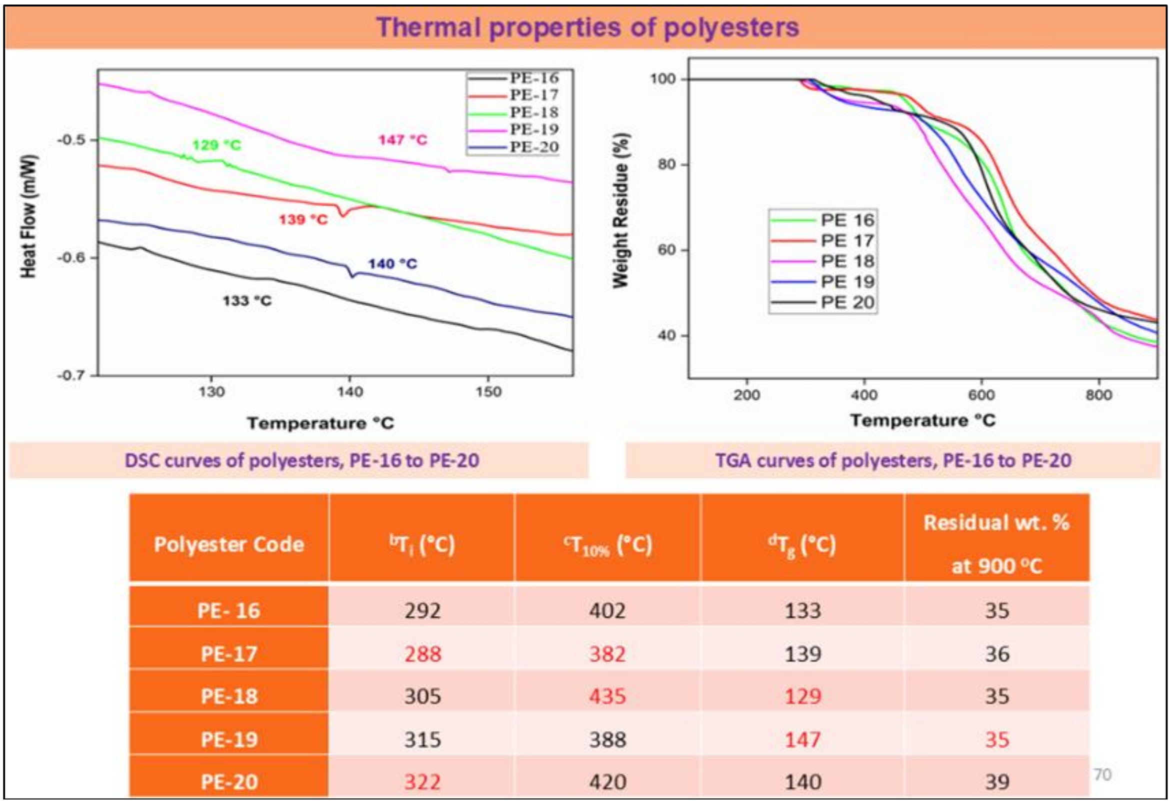


DSC curves of polyesters, PE-11 to PE-15

TGA curves of polyesters, PE-11 to PE-15

Polyester Code	$^{b}T_i$ (°C)	$^{c}T_{10\%}$ (°C)	$^{d}T_g$ (°C)	Residual wt. % at 900 °C
PE-11	280	388	116	42
PE-12	275	365	109	39
PE-13	288	402	110	49
PE-14	300	380	129	32
PE-15	305	408	125	40

Fig 3: TGA and DSC curves of polyesters, PE-11 to PE-15



Polyester Code	$^{b}T_i$ (°C)	$^{c}T_{10\%}$ (°C)	$^{d}T_g$ (°C)	Residual wt. % at 900 °C
PE- 16	292	402	133	35
PE-17	288	382	139	36
PE-18	305	435	129	35
PE-19	315	388	147	35
PE-20	322	420	140	39

Fig 4: TGA and DSC curves of polyesters, PE-16 to PE-20

3.3 Structure-Property Correlation

The combined results of the TGA and DSC analyses establish a clear correlation between pendant group orientation and thermal properties of the synthesized polyesters. The XV series, containing 1-naphthyl pendant groups, displayed lower Tg values and slightly lower char yields, which correspond to greater flexibility, enhanced chain mobility, and improved potential for solubility and processability. These characteristics are advantageous for applications where ease of fabrication, film formation, or solution processability is required.

On the other hand, the XVIII series, containing 2-naphthyl pendant groups, exhibited higher Tg values and consistently higher char yields, reflecting enhanced rigidity and superior resistance to thermal degradation. The closer chain packing promoted by the 2-naphthyl orientation results in reduced free volume, stronger intermolecular interactions, and greater stability under elevated temperatures. Such features make the XVIII polyesters more suitable for high-performance applications requiring long-term thermal endurance, such as in heat-resistant coatings, electronic substrates, and composite materials.

Thus, this comparative study reveals that pendant orientation is a decisive factor in tuning the balance between flexibility and stability in aromatic polyesters. By selecting an appropriate pendant group orientation, it is possible to rationally design materials that exhibit either enhanced process ability (XV series) or superior thermal resistance (XVIII series), depending on the intended end-use application.

4. Conclusion

In this study, two series of aromatic polyesters containing pendant naphthyl-benzamide groups were successfully synthesized through interfacial polycondensation of the diols 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl) benzamide (XV) and 3,5-dihydroxy-N-(4-(naphthalen-7-yloxy)phenyl)benzamide (XVIII) with varying ratios of isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC). The chemical structures of the diols and polyesters were confirmed by FTIR and NMR spectroscopy, while polymerization yields and inherent viscosity measurements demonstrated that moderate to high molecular weight polymers were obtained in consistently high yields.

The thermal behavior of these polyesters was systematically investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results revealed that all polyesters possessed excellent thermal stability, with decomposition onset temperatures (Ti) above 150 °C and 10% weight loss temperatures (T10) ranging from 355 to 467 °C. The XVIII-based polyesters showed higher T10 values and superior char yields compared to the XV-based series, confirming their enhanced resistance to thermal degradation. The ability of these polymers to retain a greater proportion of mass at elevated temperatures underscores the stabilizing influence of the pendant 2-naphthyl orientation.

DSC analysis provided complementary evidence of the structural influence of pendant orientation. The XV-based polyesters exhibited Tg values in the range of 109-129 °C, consistent with increased flexibility and chain mobility due to the steric disruption introduced by the pendant 1-naphthyl group. In contrast, the XVIII-based polyesters demonstrated higher Tg values, ranging from 129-147 °C, indicating more compact chain packing and reduced free volume. These findings highlight the role of 2-naphthyl substitution in promoting rigidity and restricting segmental motion, thereby enhancing the thermal resistance of the polymer matrix.

Taken together, the comparative study clearly demonstrates that pendant orientation plays a decisive role in controlling the structure-property relationships of aromatic polyesters. The XV series, with 1-naphthyl pendants, offers greater chain flexibility and potentially improved solubility and processability, making them attractive candidates for applications requiring solution processing or film formation. Conversely, the XVIII series, with 2-naphthyl pendants, provides superior thermal stability and rigidity, which are highly desirable for high-temperature and high-performance applications such as coatings, composite matrices, and advanced electronic materials.

Overall, this investigation establishes pendant orientation as a powerful structural design parameter for tailoring the balance between flexibility and stability in aromatic polyesters. The insights gained from this work open avenues for the rational design of next-generation polymeric materials with customized properties suited to diverse industrial and technological applications.

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