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Viscosity, solubility, and structural order of aromatic polyesters containing pendant naphthyl-benzamide units

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Abstract

Aromatic polyesters are valued for their thermal stability, mechanical strength, and chemical resistance but suffer from poor solubility and limited processability due to rigid backbones and strong intermolecular interactions. 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 IPC and TPC via interfacial polycondensation.

The polyesters exhibited inherent viscosities of 0.35-0.54 dL/g, confirming moderate-to-high molecular weights. They were highly soluble in polar aprotic solvents (NMP, DMF, DMSO, DMAc) but poorly soluble in chloroform and dichloromethane. XV-based polyesters showed better solubility than XVIII analogues, consistent with greater chain disruption. XRD analysis revealed amorphous structures with broad halos at $2\theta = 15\text{-}25°$, confirming reduced chain packing due to bulky pendant groups.

Overall, pendant orientation strongly influenced solubility and structural order: XV polyesters were more soluble and amorphous, whereas XVIII polyesters were more compact and less soluble. These insights highlight pendant design as a key strategy for tailoring polyesters for coatings, membranes, and composite applications.

Keywords: Aromatic polyesters, viscosity, solubility, XRD, naphthyl-benzamide, pendant orientation

Introduction

Aromatic polyesters are among the most versatile families of high-performance polymers. Their combination of high thermal resistance, chemical inertness, and mechanical durability has enabled them to find applications in fields as diverse as aerospace, electronics, coatings, packaging, and biomedical engineering. The structural backbone of aromatic polyesters, composed of rigid aromatic rings and ester linkages, imparts excellent dimensional stability and resistance to degradation under harsh conditions [1-8].

However, despite their desirable properties, conventional aromatic polyesters are often plagued by poor solubility in organic solvents and high processing temperatures. These drawbacks are a direct result of their highly rigid backbones, strong intermolecular forces, and efficient packing of chains in the solid state. Such features reduce free volume, restrict chain motion, and limit opportunities for solution-based processing and film formation. Overcoming these limitations while retaining the intrinsic high stability of aromatic polyesters remains a long-standing challenge in polymer chemistry [9-20].

One strategy to address this issue involves structural modification of the polymer backbone. Researchers have explored the incorporation of flexible ether linkages, asymmetric or non-coplanar units, cardo structures, and bulky pendant groups. Among these approaches, the introduction of bulky pendant substituents has proven particularly effective. Pendant groups disrupt intermolecular interactions, weaken chain packing, and introduce free volume, which collectively enhance solubility and improve processability. Furthermore, the size, shape, and orientation of the pendant group play crucial roles in determining the degree of disruption and the resulting macroscopic properties of the polymer [21-26].

Naphthyl-based pendant groups are of particular interest because of their extended aromatic nature and steric bulk.

The orientation of the pendant group, whether attached through the 1-position or the 2-position of the naphthalene ring, can significantly influence chain packing, rigidity, solubility, and crystallinity. Subtle changes in pendant orientation may therefore lead to measurable differences in polymer behavior [27-30].

In this study, we report a comparative investigation of two series of aromatic polyesters containing pendant naphthyl-benzamide groups. 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 derived from 2-naphthol. Both diols were synthesized and polymerized with IPC and TPC using an interfacial polycondensation method. The resulting polyesters were systematically studied for their viscosity, solubility, and degree of structural order by XRD. These three parameters are especially relevant because they provide insight into chain length, processability, and solid-state packing behavior of the polymers. The aim of this work is to elucidate how pendant group orientation affects these properties and to establish useful structure-property correlations for the design of high-performance polyesters.

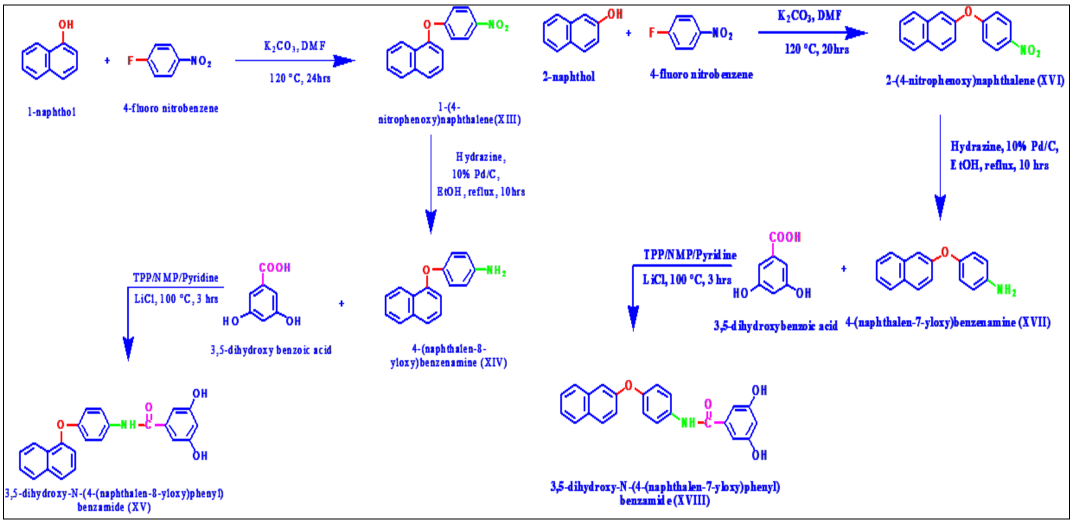
Experimental

Materials

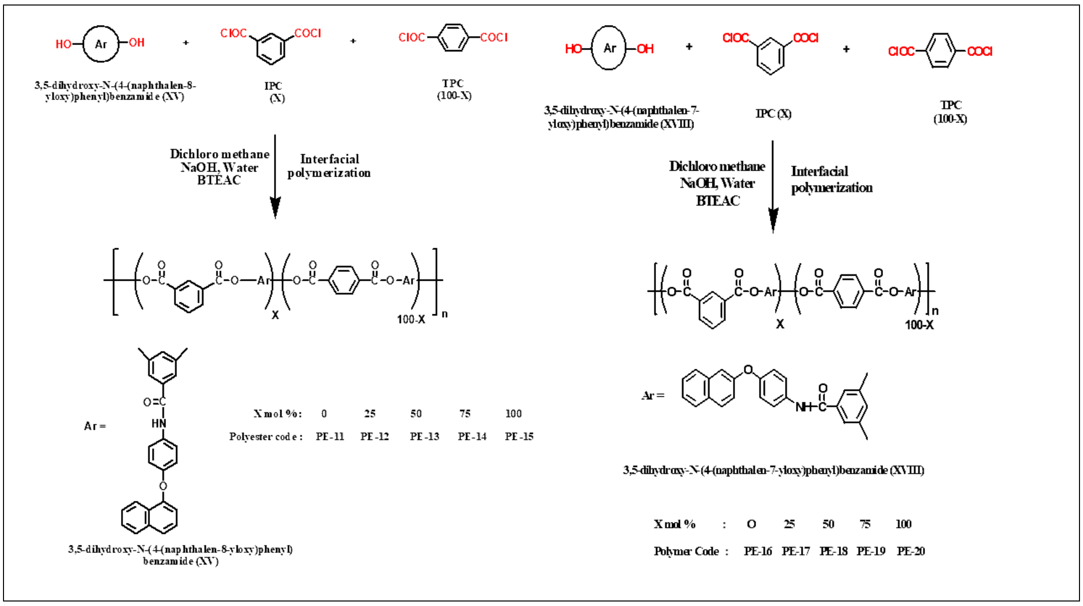
All chemicals and solvents were of analytical grade and used as received, including 1-naphthol, 2-naphthol, 4-fluoronitrobenzene, hydrazine hydrate, Pd/C, DMF, ethanol, methanol, LiCl, pyridine, NMP, triphenyl phosphate, IPC, TPC, and BTEAC. Solvents used for solubility tests included NMP, DMF, DMSO, DMAc, m-cresol, THF, $CHCl_3$, DCM, and H_2SO_4.

Synthesis of Diols and Polyesters

The diols XV and XVIII were synthesized by aromatic nucleophilic substitution of 4-fluoronitrobenzene with 1-naphthol or 2-naphthol, followed by catalytic reduction of the nitro intermediate using hydrazine hydrate and Pd/C, and subsequent condensation with 3,5-dihydroxybenzoic acid under Yamazaki phosphorylation conditions. The polyesters were obtained by interfacial polycondensation with IPC and TPC in varying molar ratios, using sodium hydroxide as a base and BTEAC as a phase-transfer catalyst. Yields exceeded 90%, and inherent viscosities were in the range of 0.35-0.54 dL/g. As shown in Scheme 1 and 2.



Scheme 1: Synthesis of Diol Monomers



Scheme 2: Synthesis of Polyesters

Characterization

The chemical structures of the synthesized diols and polyesters were confirmed by Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR, ^1H and ^13C), which verified the successful incorporation of the pendant naphthyl-benzamide units into the polymer backbones. The structures of the synthesized diols were confirmed by FTIR and NMR spectroscopy, and the corresponding spectra are presented in Figs. 1-4.

The inherent viscosities of the polyesters were determined at 30 °C using an Ubbelohde suspended-level viscometer, with measurements carried out on 0.5 g/dL solutions of the polymers in NMP.

The solubility behavior of the polymers was qualitatively assessed in a range of solvents, and the results were expressed as soluble (++), partially soluble (+-), or insoluble (--). The degree of structural ordering was examined by wide-angle X-ray diffraction (WAXD) using a Rigaku diffractometer equipped with Cu Kα radiation, recorded over a 2θ range of 5-50°.

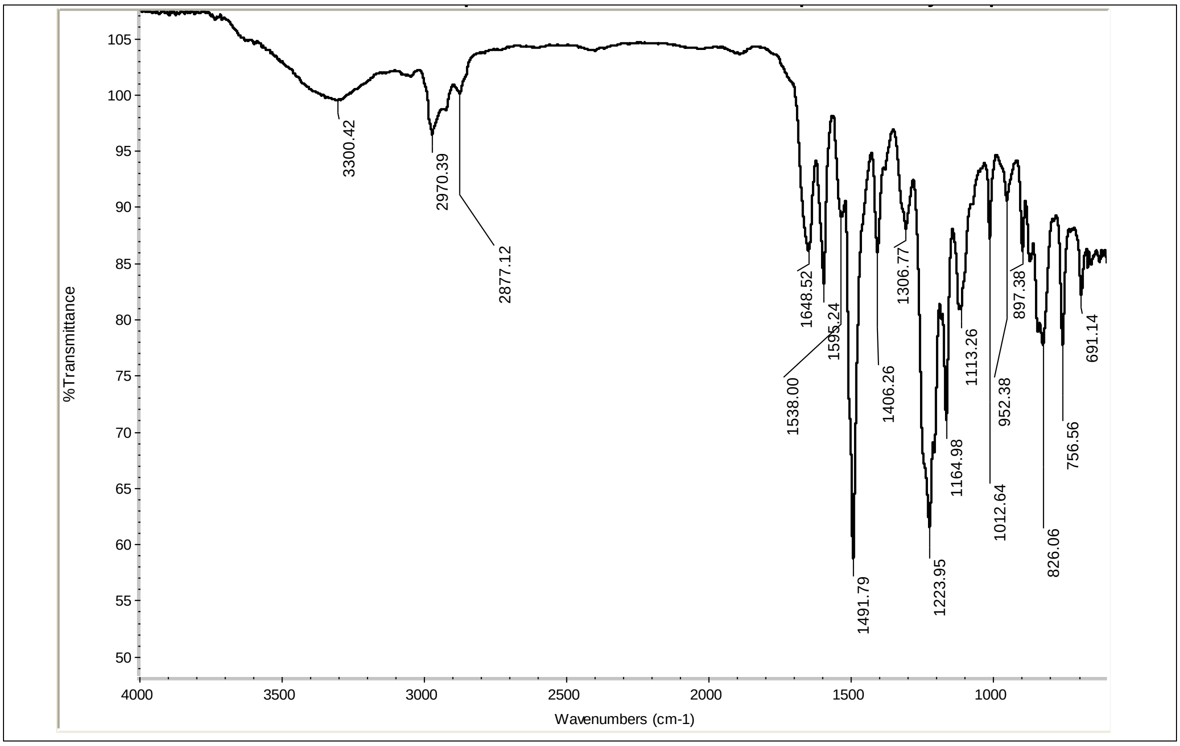


Fig 1: FT-IR spectrum of 3, 5-dihydroxy-N-(4-(naphthalen-8-yloxy) phenyl) benzamide (XV)

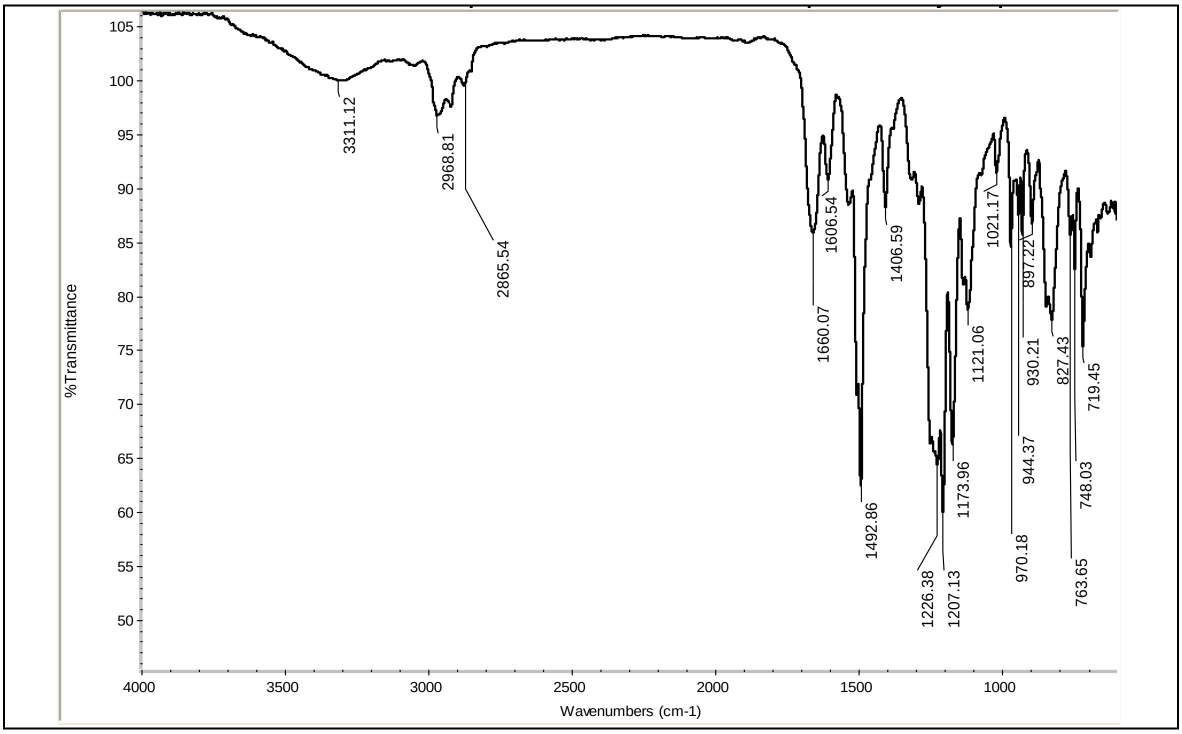


Fig 2: FT-IR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-7-yloxy) phenyl) benzamide (XVIII)

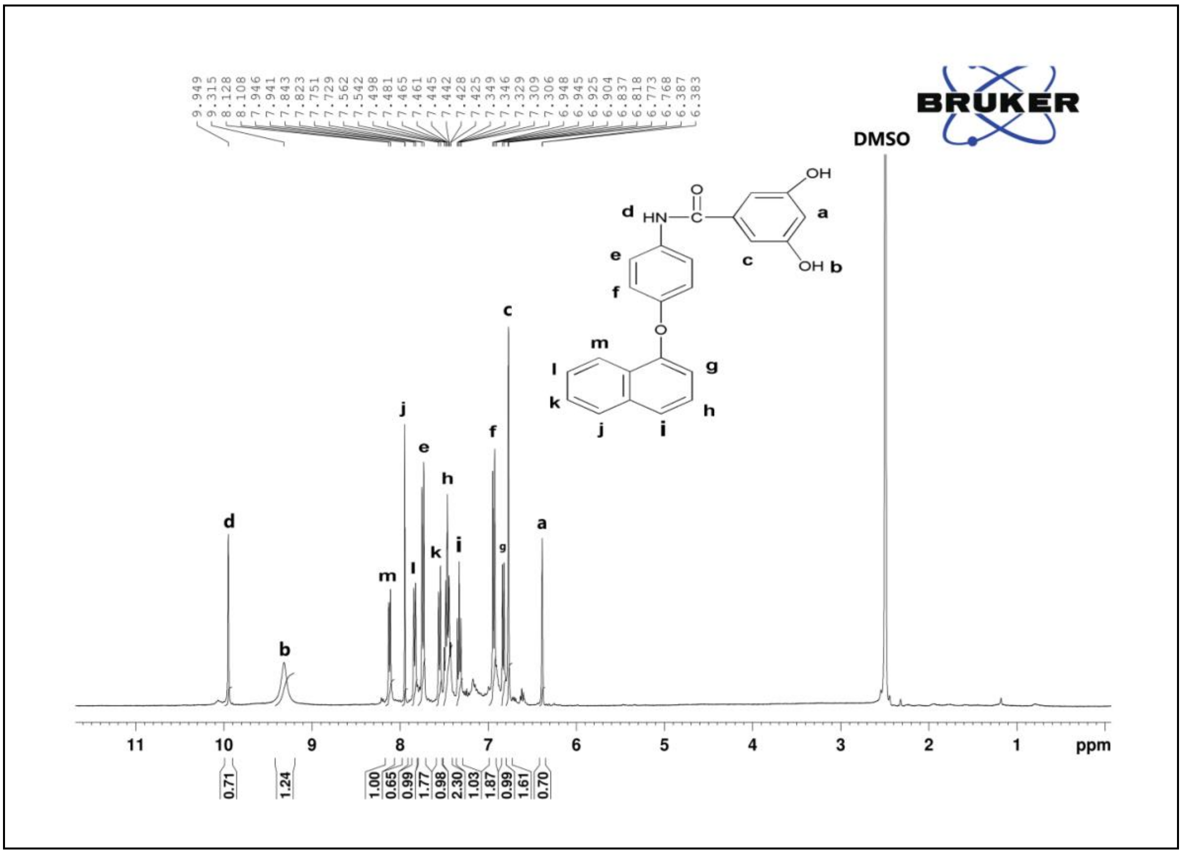


Fig 3: ^{1}H NMR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy) phenyl) benzamide (XV)

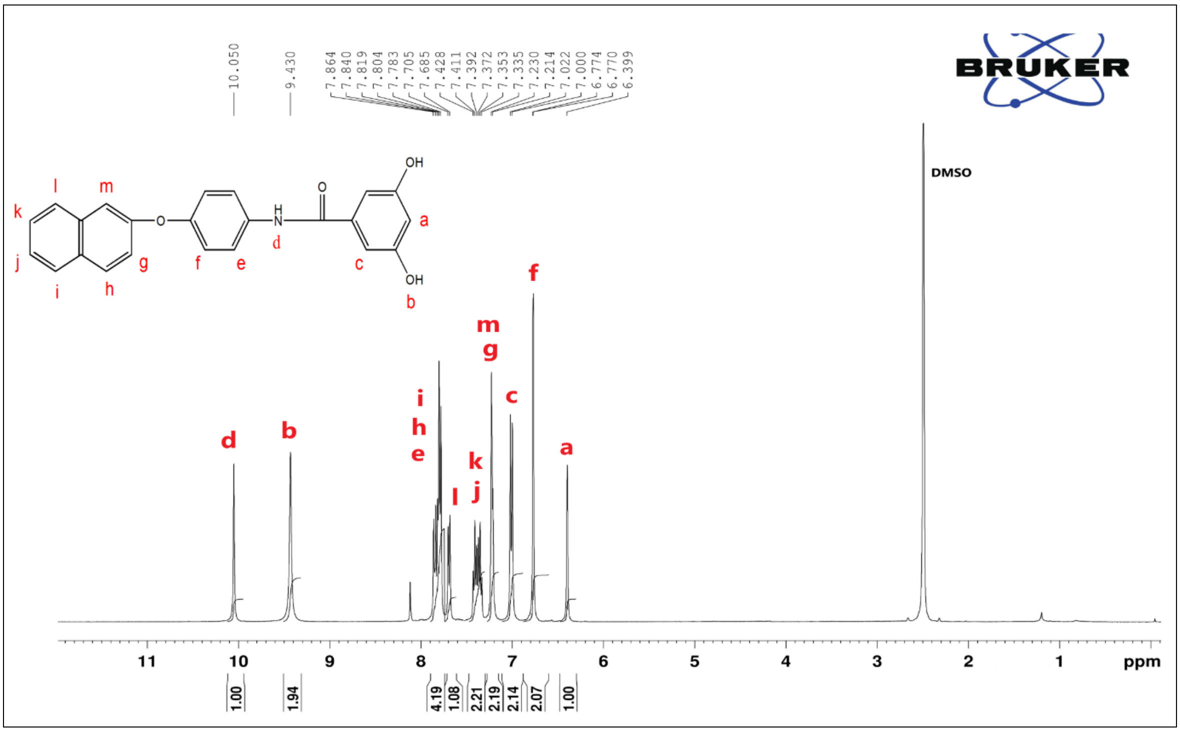


Fig 4: ^{1}H NMR spectrum of 3, 5-dihydroxy-N-(4-(naphthalen-7-yloxy) phenyl) benzamide (XVIII)

Results and Discussion

Inherent Viscosity

The inherent viscosity of a polymer solution is directly related to its molecular weight and provides valuable information about the efficiency of the polymerization reaction. The inherent viscosities of the synthesized polyesters, as summarized in Table 1, indicate the formation of polymers with moderate to high molecular weights. The XV-derived polyesters (PE-11 to PE-15) showed inherent viscosity values ranging from 0.37 to 0.54 dL/g, while the XVIII-derived polyesters (PE-16 to PE-20) exhibited slightly lower values, between 0.35 and 0.48 dL/g. These results suggest that both series achieved moderate to high molecular weight, consistent with successful interfacial polycondensation. The marginally lower viscosities of the XVIII-based series may be attributed to steric hindrance from the 2-naphthyl orientation, which slightly reduces chain growth efficiency during polymerization.

3.2 Solubility

The solubility behavior of the polyesters is summarized in Table 2. Both XV and XVIII-based polyesters dissolved readily in polar aprotic solvents such as NMP, DMF, DMSO, and DMAc, as well as in concentrated H_2SO_4, reflecting the presence of polar amide and ether functionalities in the backbone. Solubility in m-cresol was moderate, while the polymers were partially soluble or insoluble in less polar solvents such as THF, chloroform, and dichloromethane.

Between the two series, the XV-based polyesters consistently exhibited slightly better solubility compared to their XVIII counterparts. This is attributed to the 1-naphthyl orientation, which creates greater steric disruption of chain packing and provides increased free volume, thereby facilitating dissolution in organic solvents. The XVIII series, with more compact 2-naphthyl packing, showed somewhat reduced solubility. These observations highlight the sensitivity of solution properties to pendant group orientation.

Table 1: Yield and inherent viscosity of polyesters[a]

Polyester Code	Diacid Chloride Ratio (IPC: TPC, mol%)	Yield (%)	Inherent Viscosity (dL/g)
PE-11	100:0	84.4	0.37
PE-12	75:25	88.2	0.50
PE-13	50:50	92.3	0.48
PE-14	25:75	88.5	0.53
PE-15	0:100	93.2	0.54
PE-16	100:0	90.2	0.36
PE-17	75:25	91.7	0.46
PE-18	50:50	93.2	0.48
PE-19	25:75	90.5	0.45
PE-20	0:100	92.3	0.35

Table 2: Solubility of polyesters

Solvent	PE-11	PE-12	PE-13	PE-14	PE-15	PE-16	PE-17	PE-18	PE-19	PE-20
NMP	++	++	++	++	++	++	++	++	++	++
DMF	++	++	++	++	++	++	++	++	++	++
DMSO	++	++	++	++	++	++	++	++	++	++
DMAc	++	++	++	++	++	++	++	++	++	++
THF	+-	+-	++	++	++	++	++	++	++	++
m-Cresol	++	++	++	+-	++	++	++	++	+-	++
DCM	+-	+-	+-	+-	+-	+-	+-	+-	+-	+-
$CHCl_3$	+-	--	+-	+-	--	+-	+-	+-	+-	--
H_2SO_4	++	++	++	++	++	++	++	++	++	++

+ +: Soluble, +-: Partially soluble, - - Insoluble

X-ray Diffraction (XRD)

The WAXD patterns of both XV- and XVIII-based polyesters displayed broad halos in the 2θ region of 15-25°, characteristic of amorphous materials. The absence of sharp peaks confirmed that the introduction of bulky pendant naphthyl-benzamide groups disrupted chain regularity, preventing crystallization. The wide-angle X-ray diffraction (WAXD) patterns of the synthesized polyesters, as shown in Fig. 5 and 6, reveal their predominantly amorphous nature due to the disruption of regular chain packing by bulky pendant groups.

Closer examination revealed that the XV-based polyesters had slightly broader halos, indicating a higher degree of amorphousness compared to the XVIII series. The 2-naphthyl orientation in the XVIII polyesters allowed somewhat closer packing, as suggested by marginally narrower halos. These differences in XRD patterns are in good agreement with solubility data, since greater amorphous character in the XV series correlates with better solubility.

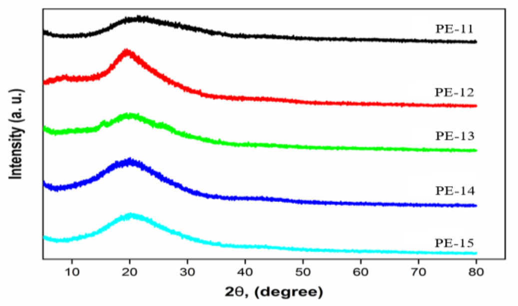


Fig 5: XRD curves of polyesters, PE-11 to PE-15

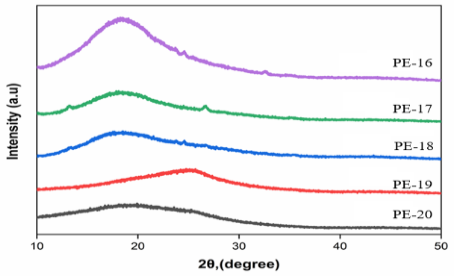


Fig 6: XRD curves of polyesters, PE-16 to PE-20

Structure-Property Correlation

By combining the results of viscosity, solubility, and XRD analyses, clear structure-property correlations emerge. The XV series, with pendant 1-naphthyl groups, exhibited slightly higher viscosities, better solubility, and greater amorphous character. This behavior is consistent with enhanced chain disruption, weaker intermolecular packing, and increased free volume. In contrast, the XVIII series, with pendant 2-naphthyl groups, displayed slightly lower viscosities, poorer solubility, and more compact packing, reflecting stronger intermolecular interactions.

These results demonstrate that pendant orientation plays a decisive role in tailoring macroscopic properties such as solubility and chain order. Even minor structural differences in pendant orientation can lead to significant changes in polymer behavior.

Conclusion

Two series of aromatic polyesters containing pendant naphthyl-benzamide groups were successfully synthesized and characterized for their viscosity, solubility, and structural order. The inherent viscosities indicated moderate to high molecular weights, while solubility tests demonstrated that both series dissolved well in polar aprotic solvents but poorly in non-polar solvents. The XV-based polyesters consistently showed slightly higher viscosities, greater solubility, and a more amorphous nature compared to the XVIII-based polyesters.

XRD confirmed that both series are largely amorphous due to the disruptive effect of bulky pendant groups, but the XV series exhibited broader halos, indicative of greater disorder. Together, these results highlight that pendant group orientation is a powerful tool for tuning the balance between solubility, processability, and structural order in aromatic polyesters. The insights from this study can guide the rational design of polyesters for specific applications, where either high solubility and processability (XV series) or greater rigidity and compact packing (XVIII series) are desired.

References

1. Morgan PW. Condensation Polymers by Interfacial and Solution Methods. Interscience, New York; 1965.
2. Seymour RB, Kirshenbaum GS, editors. High Performance Polymers: Their Origin and Development. Elsevier, New York; 1986.
3. Imai Y, Tassavori SJ. J Polym Sci Part A Polym Chem. 1984;22:1319-1325.
4. Yoneyama M, Kuruppu KDA, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem. 1989;27:979-985.
5. Yang CP, Oishi Y, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem. 1990;28:1353-1359.
6. Liau GS, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem. 1992;30:2195-2203.
7. Watanabe S, Kobayashi A, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem. 1994;32:909-916.
8. Kakimoto M, Negi YS, Imai Y. J Polym Sci Part A Polym Chem. 1986;24:1511-1519.
9. Jeong HJ, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem. 1991;29:1293-1299.
10. Jeong HJ, Oishi Y, Kakimoto M, Imai Y. J Polym Sci Part A Polym Chem. 1990;28:3293-3300.
11. Carter KR, Miller RD, Hedrick JL. Polym J. 1993;26:2209-2216.
12. Hedrick JL, Labadie JW. J Polym Sci Part A Polym Chem. 1988;21:1883-1890.
13. Hedrick JL, Labadie JW. J Polym Sci Part A Polym Chem. 1990;23:1561-1568.
14. Singh R, Hay AS. Macromolecules. 1992;25:1025-1033.
15. Connell JW, Hergenrother PM. J Polym Sci Part A Polym Chem. 1991;29:1667-1674.
16. Connell JW, Hergenrother PM, Wolf P. Polymer. 1992;33:3507-3514.
17. Smith JG, Connell JW, Hergenrother PM. Polymer. 1992;33:1742-1750.
18. Hergenrother PM, Smith JG, Connell JW. Polymer. 1993;34:856-862.
19. Bier G. Polymer. 1974;15:527-534.
20. Maresca LM, Robeson LM, Margolis JM. Aromatic Polyimides. In: Margolis JM, ed. Polyimides: Synthesis, Characterization, and Applications. Marcel Dekker, New York; 1985. p. 255-282.
21. Arroyo M, Olabisi O. Aromatic Thermoplastics. In: Olabisi O, ed. Handbook of Thermoplastics. Marcel Dekker, New York; 1997. p. 599-608.
22. Ober CK, Jin JI, Lenz RW. Adv Polym Sci. 1984;59:103-146.
23. Bucio E, Lara-Estevez JCI, Ruiz-Treviño FA, Acosta-Huerta A. Polym Bull. 2006;56:163-170.
24. Hsiao SH, Chiou JH. Polym J. 2001;33:95-101.
25. Hsiao SH, Chang HY. J Polym Res. 1995;2:99-108.
26. Loría-Bastarrachea MI, Vázquez-Torres H, Aguilar-Vega MJ. J Appl Polym Sci. 2002;86:2515-2522.
27. Liaw DJ, Hsu JJ, Liaw BY, Cheng YC. J Polym Sci Part A Polym Chem. 2000;38:4451-4456.
28. Vibhute SS, Joshi MD, Wadgaonkar PP, Patil AS, Maldar NN. J Polym Sci Part A Polym Chem. 1997;35:3227-3234.
29. Tamami B, Yeganeh H, Kohmereh GA. Eur Polym J. 2004;40:1651-1657.
30. Hsiao SH, Chiang HW. Eur Polym J. 2004;40:1691-1697.