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Structure–Property Relationships of Novel Random Aromatic Copolyesters Containing Dibenzylidenecyclohexanone Units: Influence of Molecular Weight Distribution on Thermal and Electrical Performance

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Article information **Abstract**

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Two novel random aromatic copolyesters (**V** and **VI**) containing dibenzylidenecyclohexanone units were synthesized via interfacial polycondensation and characterized by FTIR, EA, GPC, electrical conductivity measurements, and TGA. The copolyesters exhibited high molecular weights (Mn = 48,500–52,000 g mol^{-1}) and were insoluble in common organic solvents. Electrical measurements indicated insulating to semiconducting behavior with ohmic conduction. TGA results revealed excellent thermal stability, with decomposition temperatures above 369 °C and 50% weight loss occurring at 474 °C. The enhanced thermal resistance is attributed to the rigid aromatic and conjugated structures within the polymer backbone. These results demonstrate the potential of the synthesized copolyesters for high-performance and membrane-related applications

I. Introduction

Random aromatic copolyesters have attracted considerable attention owing to their versatile structure–property relationships, which enable precise tuning of thermal, mechanical, surface, and transport characteristics for advanced technological applications. The incorporation of rigid and flexible aromatic units within the polymer backbone strongly influences chain organization, intermolecular interactions, crystallization behavior, and overall material performance.[1] In particular, aromatic polyester systems are recognized for their outstanding thermal stability, mechanical robustness, and chemical resistance, attributes that originate from the presence of aromatic rings and make them attractive candidates for demanding environments such as membrane-based separation and desalination technologies. Furthermore, the molecular architecture of aromatic polyesters can be readily modified through the introduction of functional groups or structurally rigid moieties, providing opportunities to optimize physicochemical properties and optimize performance for specific applications.[2,3]

Among various structural modifications, the incorporation of conjugated diarylidene ketone units such as dibenzylidenecyclohexanone derivatives has proven effective in enhancing chain rigidity and restricting rotational freedom along the polymer backbone.[4,5] These rigid segments

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increase steric constraints and alter molecular packing, thereby influencing thermal transitions, surface characteristics, and mechanical behavior. Such molecular-level modifications are particularly important because polymer performance is governed not only by chemical composition but also by factors related to chain architecture and molecular weight distribution. Recent studies have demonstrated that polydispersity can significantly affect crystallization processes, free-volume distribution, thermal stability, and mechanical response, often exhibiting a stronger influence on material performance than average molecular weight alone[6,7]

Accordingly, the present work investigates the combined influence of molecular weight distribution and rigid dibenzylidenecyclohexanone-based segments on the properties of three newly synthesized random aromatic copolyesters prepared via interfacial polycondensation. A comprehensive characterization approach was employed to establish detailed structure–property relationships, with particular emphasis on understanding how backbone rigidity and polydispersity collectively govern thermal behavior, surface properties, and mechanical performance. The findings provide valuable insights for the rational design of advanced aromatic polyester materials with enhanced functionality and potential applicability in high-performance separation and membrane technologies.[8]

II. Experimental

2.1 Materials

All chemicals were of high purity and were further purified using standard procedures, except for isophthaloyl chloride, which was purified by recrystallization from *n*-hexane.

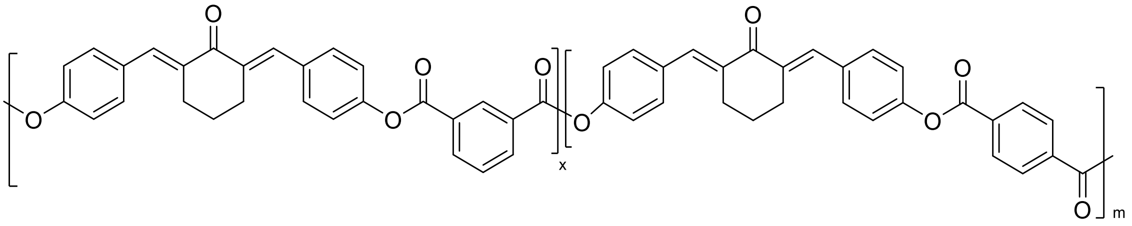
2.2 Synthesis of Dibenzylidenecyclohexanone derivatives I, II

The procedure of preparing the diphenol derivatives **I, II** has been published in a previous study.[9,10]

2.3 Synthesis of Copolyesters V – VI

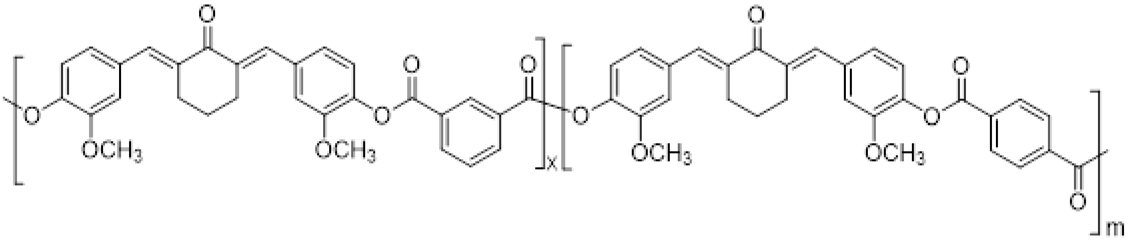
Copolyesters **V–VI** were prepared via an interfacial polycondensation process using a simple reaction apparatus consisting of a two-necked round-bottom flask. One neck was connected to a mechanical stirrer operating at 2000 rpm, whereas the second neck was fitted with a dropping funnel. A solution containing the corresponding diacid chlorides, namely (isophthaloyl dichloride **III** and/or terephthaloyl dichloride **IV**) (0.002 mol), dissolved in 25 mL of dichloromethane, was gradually added to a stirred alkaline solution of dibenzylidenecyclohexanone derivatives **I** and **II** (0.002 mol). The alkaline phase was prepared by dissolving sodium hydroxide (0.004 mol) in 50 mL of distilled water, followed by the addition of 25 mL of dichloromethane after complete dissolution of the base. The addition of the diacid chloride solution was carried out at ambient temperature over approximately 2 min under continuous stirring. After the addition was completed, the reaction mixture was maintained under vigorous stirring for an additional 1 h, resulting in the formation of copolyesters **V–VI** as lumpy precipitates. The obtained products were isolated by vacuum filtration, washed thoroughly with distilled water and hot ethanol to remove impurities, and finally dried in an oven at 80 °C for 24 h.

2.3.1 Synthesis of Copolyester V



Obtained utilising the above procedure with (0.001 mol) 2,6-bis(4-hydroxybenzylidene) cyclohexanone **I** and (0.001 mol) 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** and (0.002 mol) isophthaloyl dichloride **III** as a orange lumpy precipitate with a yield of **87%**. mp >350 °C; IR: (ATR, cm^{-1}) 1741, 1669, 1600, 1156; Found: C, 74.14%; H, 4.58%. Calc. for ($C_{58}H_{44}O_{12}$): C, 77.67%; H, 4.62%.

2.3.2 Synthesis of Copolyester VI



Obtained utilising the above procedure with (0.001 mol) 2,6-bis(4-hydroxybenzylidene) cyclohexanone **I** and (0.001 mol) 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** and (0.002 mol) terephthaloyl dichloride **IV** as a yellowish lumpy precipitate with a yield of **94%**.

mp >350 °C; IR (ATR, cm^{-1}) 1739, 1668, 1598, 1154 cm^{-1}; Found: C, 72.09%; H, 4.69%. Calc. for $C_{58}H_{44}O_{12}$: C, 74.57%; H, 4.87%.

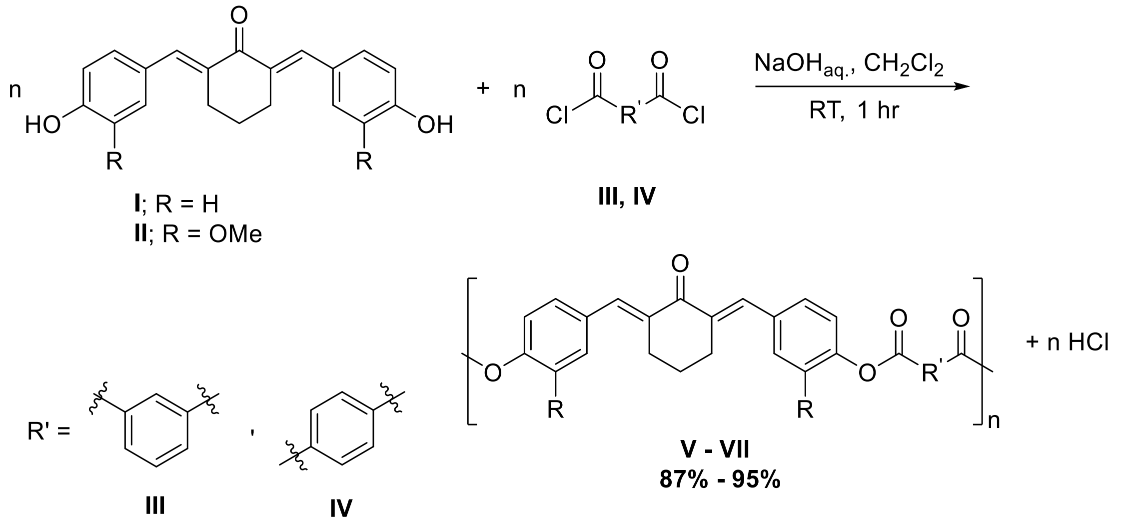
2.4 Characterization Techniques

- Electrical conductivity: measured to evaluate the electrical behavior of the copolyesters at room temperature.
- Gel permeation chromatography (GPC): employed to determine the molecular weight averages of the copolyesters.
- Thermogravimetric analysis (TGA): employed to investigate the thermal degradation behavior and evaluate the thermal stability of the synthesized copolyesters

III. Results and Discussion

3.1 Synthesis of Copolyesters V – VI

An unreported series of random copolyesters **V** – **VI** was synthesized via the interfacial polycondensation of 2,6-bis(4-hydroxybenzylidene) cyclohexanone **I** and 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** and isophthaloyl dichloride **III** and (or) terephthaloyl dichloride **IV** at room temperature (Scheme 1).



Scheme 1: synthesis of two random copolyesters **V - VI**

The chemical structures of the synthesized copolyesters were verified through a combination of Fourier-transform infrared (FTIR) spectroscopy and elemental analysis. The FTIR spectra revealed the complete disappearance of the hydroxyl stretching vibration characteristic of the precursor monomers, confirming successful polymerization. Simultaneously, new absorption bands appeared in the range of 1736–1740 cm^{-1}, attributable to ester carbonyl (C=O) groups, while bands observed at 1666–1669 cm^{-1} and 1154–11589 cm^{-1} were assigned to conjugated .carbonyl functionalities and C–O–C stretching vibrations, respectively

The elemental analysis data showed good agreement with the calculated values for the proposed repeating units of the copolyesters, supporting the assigned molecular structures. Small discrepancies between the experimental and theoretical elemental compositions, not exceeding 0.59%, were detected and are likely associated with traces of residual solvent entrapped within the polymer network during synthesis and subsequent processing steps.

3.2 Study the Solubility of Copolyesters V – VI

The room-temperature solubility of copolyesters **V – VI** was evaluated in a range of solvents, including acetone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dichloromethane (DCM), chloroform, carbon tetrachloride, 1,4-dioxane, and formic acid, using a sample concentration of 0.02 g in 3 mL of solvent. The results indicated that all copolyesters were insoluble in the tested solvents (Table 1).[11]

Table 1. Solubility Characteristics of Copolyesters **V – VI**

Solvent	Copolyester **V**	Copolyester **VI**	**Solvent**	Copolyester **V**	Copolyester **VI**
Acetone	-	-	**DCM**	-	-
1,4-Dioxane	-	-	**DMF**	-	-
$CHCl_3$	-	-	**DMSO**	-	-
CCl_4	-	-	**Formic acid**	-	-
THF	-	-			

(-) insoluble

The insolubility of the copolyesters prepared in this study can be attributed to the possible formation of copolyester chains with high molecular weights.

3.3 Electrical Conductivity of Copolyesters V – VI

The electrical behavior of the synthesized copolyesters was examined using current–voltage (I–V) measurements performed on compressed disc-shaped samples at room temperature. In both cases, a linear dependence between current and applied voltage was observed, confirming ohmic conduction. Copolyester **V** (disc radius 3 mm, thickness 4.06 mm) exhibited a resistance of 4×10^9 Ω, corresponding to a resistivity of 2.784×10^9 Ω·cm and an electrical conductivity of 3.59×10^{-10} $\Omega^{-1}\cdot\text{cm}^{-1}$. By comparison, copolyester **VI** (radius 3 mm, thickness 2.71 mm) showed a markedly lower resistance of 3×10^9 Ω, with a resistivity of 3.128×10^9 Ω·cm and a higher conductivity of 4.94×10^{-9} $\Omega^{-1}\cdot\text{cm}^{-1}$.According to conventional resistivity classifications, copolyester **V** can be categorized as an electrical insulator, whereas copolyester **VI** lies within the semiconducting range. Overall, both materials demonstrate high resistivity values typical of aromatic polymer systems, with copolyester **VI** exhibiting relatively enhanced charge transport properties.[10,11]

3.4 Gel Permeation Chromatography of Copolyesters V – VI

Gel permeation chromatography (GPC) was used to evaluate the molecular weight characteristics of copolyesters **V** and **VI**. Both polymers exhibited relatively high molecular weights, indicating efficient polymerization and good chain growth. Copolyester **V** showed Mn = 52,000 g/mol and Mw = 98,800 g/mol with a polydispersity index (PDI, which measures the breadth of the molecular weight distribution) of 1.90, while copolyester **VI** gave Mn = 48,500 g/mol and Mw = 97,000 g/mol with PDI = 2.00. The slightly lower molecular weight of **VI** may be attributed to the influence of methoxy group incorporation. Overall, both polymers show suitable molecular weight distributions for high-performance membrane applications.[12,13,14]

3.5 Thermogravimetric Analysis (TGA) V – VI

The thermal stability of copolyesters **V** and **VI** was evaluated by thermogravimetric analysis (TGA), and the corresponding thermograms are presented in Figures 1 and 2. Both copolyesters exhibited high thermal stability, with decomposition occurring at elevated temperatures. Copolyester **V** showed a 10% weight loss at 369 °C, while 20%, 30%, 40%, and 50% weight losses were observed at 423, 449, 461, and 474 °C, respectively. In comparison, copolyester **VI** exhibited a slightly higher initial decomposition temperature, reaching 10% weight loss at 373 °C. The temperatures corresponding to 20%, 30%, 40%, and 50% weight losses were 417, 440, 458, and 474 °C, respectively. The TGA results indicate that copolyester **VI** possesses slightly greater resistance to the onset of thermal degradation, whereas copolyester **V** demonstrates marginally higher stability at intermediate stages of decomposition. Despite these differences, both copolyesters exhibited comparable thermal stability at higher temperatures, reaching 50% weight loss at 474 °C. The excellent thermal stability observed for both materials can be attributed to the aromatic polyester backbone and the presence of rigid conjugated structural units, which enhance chain rigidity and intermolecular interactions, thereby improving resistance to thermal decomposition.[15,15,6]

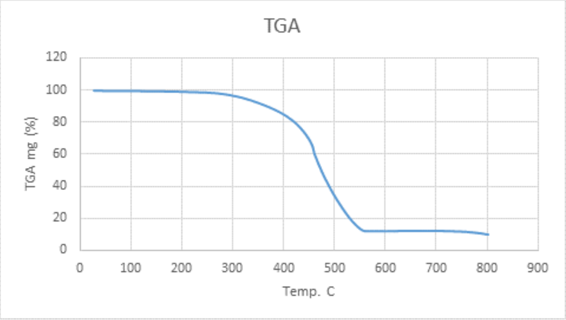


Figure 1. Thermogravimetric curve of copolyester **V**

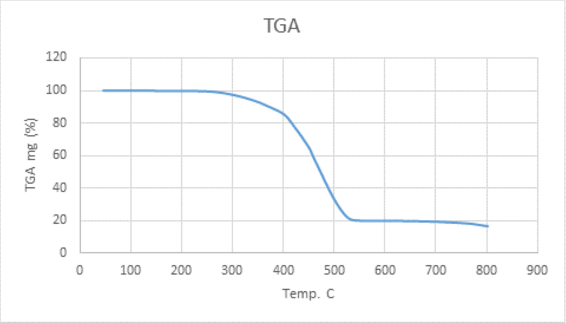


Figure 2. Thermogravimetric curve of copolyester **VI**

IV. Conclusions

Two new aromatic copolyesters containing rigid dibenzylidenecyclohexanone units were successfully synthesized by interfacial polycondensation. The polymers exhibited high molecular weights, complete insolubility in the tested solvents, and good thermal stability with decomposition temperatures above 369 °C. Electrical measurements indicated that copolyester **VI** displaying slightly higher conductivity than copolyester **V**. The combination of high thermal stability and favorable physicochemical properties suggests that these materials are promising candidates for advanced engineering and membrane applications.

V. References

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[1] Yahia, M.; Refaat, D.; El-Enany, G. and Abd El-Ghaffar, M. A. Electrical Properties of Chelating Copolymers and Their Metal Complexes: Binary Chelating Copolymers of Styrene with Organic Acids. *J. Basic Appl. Sci.* **2024**, *13*, 128.

[2] Brown, T., Patel, S. and Morgan, K. Molecular Weight Distribution Effects in Polyesters, *Macromolecules*, **2018**, 51(2), 730–742.

[3] Ahmed, M. and Lee, D. Correlation between PDI and Polymer Crystallization Kinetics, *Polymer Journal*, **2017**, 49(9), 1123–1134.

[4] Silva, R. and Barbosa, L. GPC Analysis of Aromatic Copolyesters, *Journal of Applied Polymer Science*, 2016, 133(45), 441–452.

[5] Park, Y. and Jeong, D. Thermal Behavior of Polyesters with Controlled PDI, *Thermochimica Acta*, **2016**, 642, 1–10.

[6] Prasad, V. S. and Pillai, K. S. Synthesis and thermal behavior of thermotropic terpolymers based on substituted aromatic units. J. Appl. Polym. Sci. 2001, 82, 1021–1029.

[7] Hina, S.; Zhang, Y.; Wang, H. Characterization of polymeric solutions: a brief overview. *Rev. Adv. Mater. Sci.* **2014**, 36, 165–176.

[8] Abd-Alla, M. A.; Ismail, M.T. and El-Khawaga, A.M. Revue Roumiane de Chimie, 1985, 30 (4), 343.

[9] Kamal, I. A.; Hammam, A. S.; Radwan, S. M. and Abdel-Rahman, M. A. New Unsaturated Copolyesters Based on Diarylidenecyclopentanone: Optimum Conditions of Synthesis, Characterization and Morphology, *International Journal of Basic & Applied Sciences IJBAS-IJENS*, **2011**, 11 (04), 15–35.

[10] Odian, G. and Imre, K. J. Kinetics of step-growth polymerization. *J. Polym. Sci., Polym. Chem. Ed.*, **1980**, 18, 737–748.

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[11] Yahia, M.; Refaat, D.; El-Enany, G. and Abd El-Ghaffar, M. A. Electrical Properties of Chelating Copolymers and Their Metal Complexes: Binary Chelating Copolymers of Styrene with Organic Acids. *J. Basic Appl. Sci.* **2024**, *13*, 128.

[12] Brown, T., Patel, S. and Morgan, K. Molecular Weight Distribution Effects in Polyesters, *Macromolecules*, **2018**, 51(2), 730–742.

[13] Ahmed, M. and Lee, D. Correlation between PDI and Polymer Crystallization Kinetics, *Polymer Journal*, **2017**, 49(9), 1123–1134.

[14] Silva, R. and Barbosa, L. GPC Analysis of Aromatic Copolyesters, *Journal of Applied Polymer Science*, **2016**, 133(45), 441–452.

[15] Abd-Alla, M. A. and Aly, K. I. Arylidene Polymers XIII—Synthesis, Characterization and Morphology of New Unsaturated Polycarbonates via Phosgenation of Diarylidenecycloalkanones. *High Perform. Polym.* **1990**, 2(4), 223–234.

[16] Park, Y. and Jeong, D. Thermal Behavior of Polyesters with Controlled PDI, *Thermochimica Acta*, **2016**, 642, 1–10.

[17] Ghosh, P. DSC Analysis of Random Aromatic Polyester Blends, *Journal of Thermal Analysis and Calorimetry*, **2017**, 128(3), 1553–1565.

العلاقات بين التركيب والخواص في بولي إسترات أروماتية مشتركة عشوائية جديدة تحتوي على وحدات ثنائي بنزيليدين سيكلوهكسانون: تأثير توزيع الأوزان الجزيئية على الأداء الحراري والكهربائي

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الملخص

تم تحضير بولي إسترين عطريين مشتركين عشوائيين جديدين (**V** و**VI**) يحتويان على وحدات ثنائي بنزيليدين سيكلوهكسانون بطريقة البلمرة بالتكاثف البيني، وتم توصيفهما باستخدام مطيافية الأشعة تحت الحمراء (FTIR)، والتحليل العنصري، وكروماتوغرافيا النفاذ الهلامي (GPC)، وقياسات التوصيلية الكهربائية، والتحليل الوزني الحراري (TGA). أظهرت البوليمرات المحضرة أوزانًا جزيئية مرتفعة (Mn = 48,500–52,000 غ/مول) وعدم ذوبانية في المذيبات العضوية الشائعة. وبينت القياسات الكهربائية سلوكًا يتراوح بين العزل وشبه التوصيل مع انصياع لقانون أوم. كما أظهرت نتائج التحليل الوزني الحراري ثباتًا حراريًا ممتازًا، حيث بدأت عملية التحلل عند درجات حرارة أعلى من 369 °م، ووصل فقدان الوزن إلى 50% عند 474 °م. ويُعزى هذا الثبات الحراري المرتفع إلى وجود التراكيب العطرية والمترافقة الصلبة ضمن السلسلة البوليمرية. وتشير النتائج إلى أن هذه البوليمرات المشتركة تمتلك إمكانات واعدة للاستخدام في التطبيقات عالية الأداء وتقنيات الأغشية والفصل.

معلومات مقالة

الكلمات المفتاحية

كوبوليسترات عشوائية؛ علاقة البنية بالخواص؛ خصائص حرارية وكهربائية

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