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Design and Characterization of High-Performance Random Copolyesters Based on Dibenzylidenecyclohexanone Derivatives

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Article information

Abstract

Key words

Random copolyesters; structure–property; relationship

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A new series of random copolyesters **V–VII** was synthesized via interfacial polycondensation of dihydroxybenzylidene cyclohexanone derivatives with isophthaloyl and/or terephthaloyl dichlorides. The structures were confirmed by IR spectroscopy and elemental analysis, showing characteristic ester carbonyl bands. All copolyesters were insoluble in common organic solvents, indicating high molecular weight and ordered structures. Electrical measurements classified **V** and **VII** as insulators and **VI** as a semiconductor. Thermal analysis (TGA and DSC) revealed that **VI** had the highest initial thermal stability (374 °C), **V** the highest final stability (490 °C), and **VII** the highest Tg (68 °C) and Tm (235 °C), with increasing crystallinity from 32% to 37%, confirming that enhanced molecular regularity improves both thermal stability and crystallinity.

I. Introduction

Random aromatic copolyesters continue to attract significant interest due to their tunable structure–property relationships, enabling customization of thermal, mechanical, and interfacial behaviors for advanced applications. The random incorporation of rigid and flexible segments along the polymer backbone critically influences chain packing, crystallization kinetics, and bulk performance. Incorporation of conjugated diarylidene ketone moieties into polyester chains, such as dibenzylidenecyclohexanone derivatives, has been shown to enhance backbone rigidity and thermal resistance, potentially improving structure–property correlations compared with less constrained analogues.[1,2,3]

Dibenzylidenecyclohexanone serves as a rigid, conformationally constrained building block that increases steric hindrance and reduces rotational freedom, which can profoundly affect molecular packing and morphologies in copolyester systems.[4,5] However, beyond monomer design, molecular weight distribution is now recognized as a decisive factor governing polymer performance, often exerting a greater influence than absolute molecular weight on crystallization behavior, thermal transitions, and mechanical properties. This highlights the need to systematically understand how polydispersity and rigid aromatic segments collectively tailor material properties.[6,7]

Accordingly, this work aims to elucidate the combined effects of molecular weight distribution and rigid dibenzylidenecyclohexanone segments on the structural, thermal, surface, and mechanical properties of three random aromatic copolyesters synthesized via interfacial polycondensation. A comprehensive characterization strategy was implemented to establish robust structure–property correlations and to emphasize the dominant role of the polydispersity index in directing overall material performance and enabling future design of advanced copolyester systems.

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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.

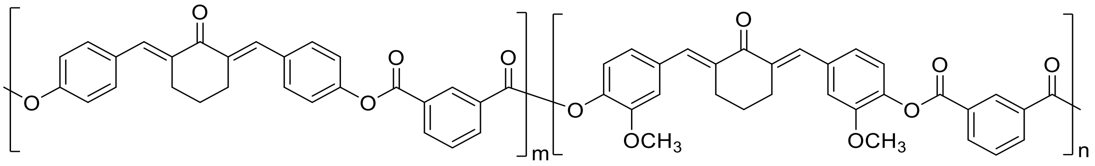
2.2 Synthesis of Dibenzylidenecyclohexanone derivatives I, II

The procedure of preparing the diphenol derivatives **I, II** has been published in a previous study.[8]

2.3 Synthesis of Copolyesters V – VII

The copolyesters **V** – **VII** were synthesized using a straightforward experimental setup comprising a two-necked round-bottom flask. One neck was fitted with a mechanical stirrer operating at 2000 rpm, while the other was equipped with an addition funnel. A solution of the appropriate diacid chlorides (isophthaloyl dichloride **III** and (or) terephthaloyl dichloride **IV**) (0.002 mol), dissolved in 25 ml of dichloromethane, was slowly introduced into a mixture containing dibenzylidenecyclohexanone derivatives **I** and **II** (0.002 mol) dissolved in an aqueous sodium hydroxide solution (0.004 mol in 50 ml of distilled water), to which 25 ml of dichloromethane had been added after complete dissolution. The addition was performed at room temperature under continuous stirring over a period of 2 min. Upon completion of the diacid chloride addition, the reaction mixture was vigorously stirred for a further 1 hr, leading to the formation of lumpy copolyester products **V** – **VII**. The resulting solids were collected by vacuum filtration, thoroughly washed with distilled water followed by hot ethanol, and subsequently dried in an oven at 80 °C for 24 hr.

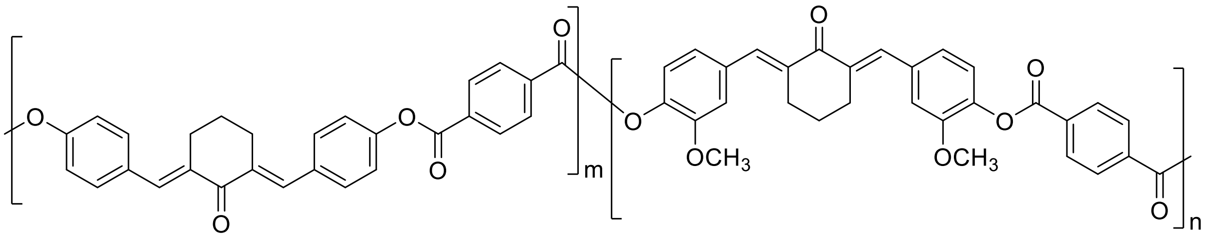
2.3.1 Synthesis of Copolyester V



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 yellowish 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, 74.67%; H, 4.75%.

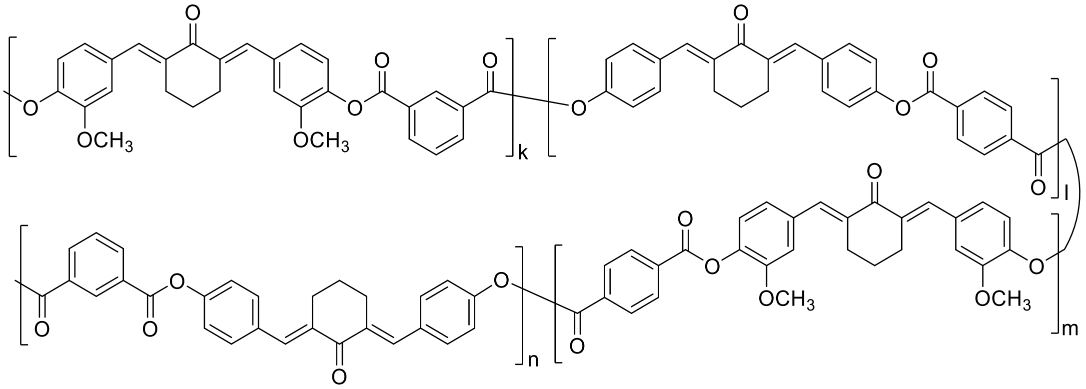
2.3.2 Synthesis of Copolyester VI



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 **93%**.
mp >350 °C; IR (ATR, cm^{-1}) 1736, 1668, 1599, 1157 cm^{-1}; Found: C, 74.39%; H, 4.67%. Calc. for $C_{58}H_{44}O_{12}$: C, 74.67%; H, 4.75%.

2.3.3 Synthesis of Copolyester VII



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 (0.001 mol) isophthaloyl dichloride **III** and (0.001 mol) terephthaloyl dichloride **IV** as a yellowish lumpy precipitate with a yield of **95%**.
mp >350 °C; IR (ATR, cm^{-1}) 1737, 1667, 1598, 1158 cm^{-1}; Found: C, 74.09%; H, 4.59%. Calc. for $C_{58}H_{44}O_{12}$: C, 74.67%; H, 4.75%.

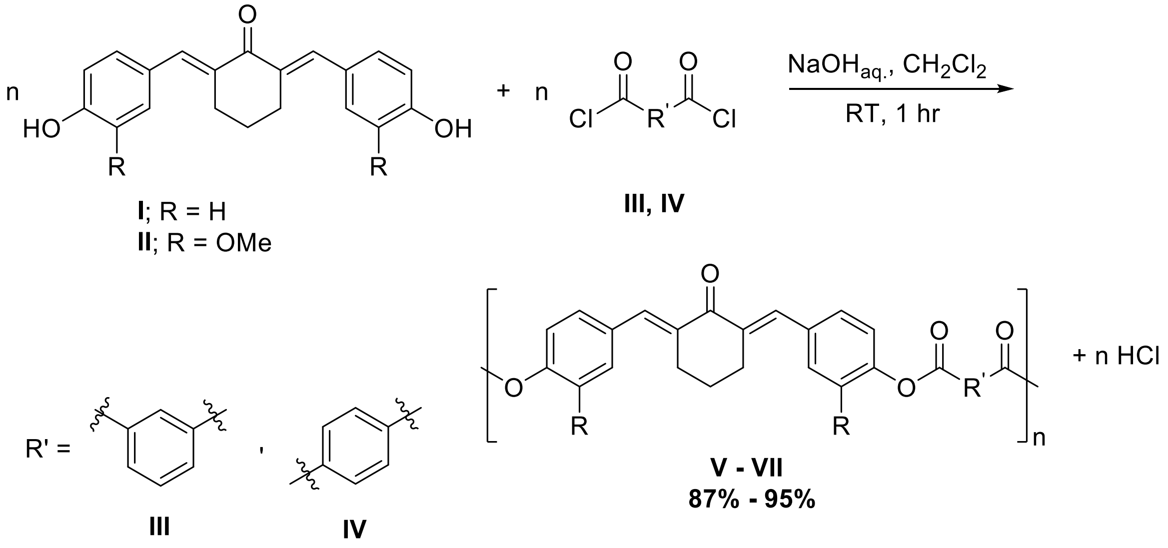
2.4 Characterization Techniques

- 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) and differential scanning calorimetry (DSC): utilized to examine thermal transitions, decomposition behavior, and overall thermal stability of the copolyester samples.

III. Results and Discussion

3.1 Synthesis of Copolyesters V – VII

An unreported series of random copolyesters **V** – **VII** 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 three random copolyesters **V - VII**

The chemical structures of the prepared copolyesters were confirmed by IR spectroscopy and elemental analysis. The IR spectra of all samples exhibited the disappearance of the characteristic O–H stretching band, along with the emergence of new absorption bands at 1736–1741 cm^{-1} corresponding to ester carbonyl groups, 1667–1669 cm^{-1} for conjugated carbonyl groups and 1156–1158 cm^{-1} for C–O–C stretching vibrations.

Elemental analysis results were consistent with the expected compositions of the repeating units in each copolyester. Minor deviations of up to 0.58% from the theoretical values were observed, which can be attributed to the common phenomenon of solvent molecules being retained within the polymer matrix during synthesis or processing.[9]

3.2 Study the Solubility of Copolyesters V – VII

The room-temperature solubility of copolyesters **V** – **VII** 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).[10]

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

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

(-) 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 – VII

The electrical properties of the prepared copolyesters were evaluated by measuring the current–voltage (I–V) relationship of compressed disc-shaped samples at room temperature. A linear V–I relationship was observed for all samples, indicating ohmic behavior.

For copolyester **V** (disc radius 3 mm, thickness 3.47 mm), a resistance of $5 \times 10^9\ \Omega$ was measured, corresponding to a resistivity of $4.072 \times 10^9\ \Omega\cdot$cm and a calculated electrical conductivity of $2.46 \times 10^{-10}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$. Copolyester **VI** (radius 3 mm, thickness 2.79 mm) showed a resistance of $2 \times 10^8\ \Omega$, yielding a resistivity of $2.026 \times 10^8\ \Omega\cdot$cm and a conductivity of $4.94 \times 10^{-9}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$. Copolyester **VII** (radius 3 mm, thickness 3.05 mm) exhibited a resistance of $1 \times 10^{10}\ \Omega$, resulting in a resistivity of $9.27 \times 10^9\ \Omega\cdot$cm and a conductivity of $1.08 \times 10^{-10}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$.

According to standard classifications based on resistivity at room temperature (conductors: $\rho < 10^{-2}\ \Omega\cdot$cm; semiconductors: $\rho \approx 10^{-2}$–$10^9\ \Omega\cdot$cm; insulators: $\rho > 10^9\ \Omega\cdot$cm), copolyesters **V** and **VII**, with resistivities above $10^9\ \Omega\cdot$cm, are categorized as electrical insulators, whereas copolyester **VI**, with a resistivity below $10^9\ \Omega\cdot$cm, lies within the semiconducting range. Overall, the prepared copolyesters exhibit high resistivity characteristic of polymeric insulating materials, with potential applications where electrical insulation is required.[11]

3.4 Gel Permeation Chromatography of Copolyesters V – VII

GPC analysis of copolyesters **V** – **VII** was not feasible due to incomplete dissolution and the formation of stable dispersions. This behavior indicates very high molecular weights and/or strong intermolecular interactions and highly ordered structures, with copolyester **VII** showing the lowest solubility. The limited solubility suggests enhanced thermal, mechanical, and chemical stability, while restricting solution-based processing.[12,13,14]

3.5 Thermal Properties of Copolyesters V – VII

The Thermogravimetric Analysis (TGA) (Figures 1 – 3) and Differential Scanning Calorimetry (DSC) (Figure 4) results reveal a clear correlation between the thermal stability and crystallization behavior of copolyesters **V**, **VI**, and **VII**. Copolyester **VI** exhibited the highest initial thermal stability, with a 10% weight-loss temperature of 374 °C, whereas copolyester **V** showed superior final stability, reaching 490 °C at 50% degradation. In contrast, copolyester **VII** displayed a lower onset degradation temperature (349 °C) but the highest glass-transition temperature (Tg = 68 °C) and melting temperature (Tm = 235 °C). Copolyester **V** showed the lowest Tg (62 °C) and a double melting endotherm at 223 and 227 °C, indicating structural heterogeneity. The melting enthalpy increased from 45 to 52 J g^{-1} and crystallinity from 32% to 37% from **V** to **VII**, explaining the observed differences in thermal degradation behavior. These findings confirm that enhanced molecular regularity improves crystalline characteristics while maintaining high thermal stability.[15,16,17]

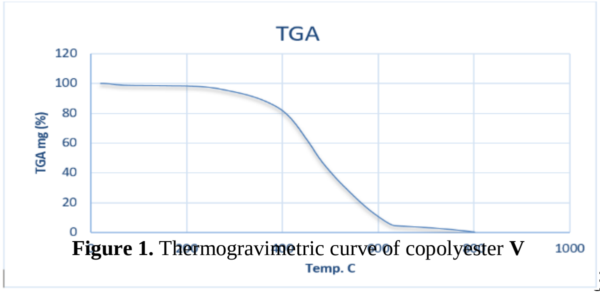
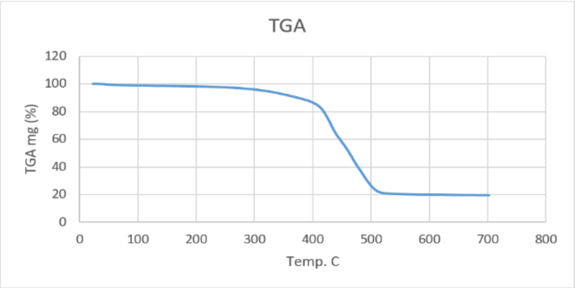


Figure 1. Thermogravimetric curve of copolyester **V**



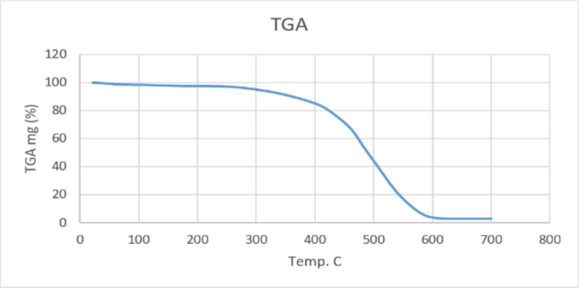


Figure 3. Thermogravimetric curve of copolyester **VII**

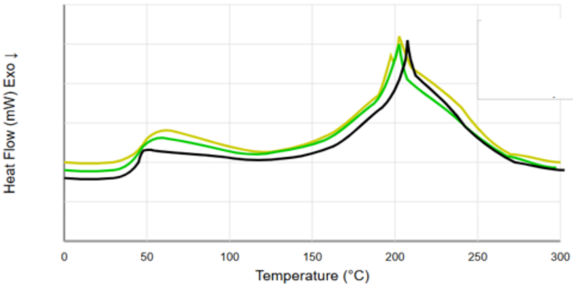


Figure 4. DSC thermograms for copolyesters **V**, **VI**, **VII**

IV. Conclusions

A series of random copolyesters **V–VII** based on dibenzylidenecyclohexanone derivatives was successfully synthesized by interfacial polycondensation and confirmed by IR spectroscopy and elemental analysis. The copolyesters exhibited very high molecular weights and ordered structures, as reflected by their complete insolubility and the failure of GPC analysis. Electrical measurements classified copolyesters **V** and **VII** as insulators, while **VI** showed semiconducting behavior, demonstrating the effect of diacid chloride composition on electrical properties. Thermal analyses revealed excellent stability for all samples, with **VI** showing the highest initial degradation temperature and **V** the highest final thermal stability. Copolyester **VII** exhibited the highest Tg and Tm values. The increase in melting enthalpy and crystallinity from **V** to **VII** confirms that enhanced molecular regularity improves crystalline order and thermal performance.

V. References

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تصميم وتوصيف كوبولي استرات عشوائية عالية الأداء مبنية على مشتقات ثنائي بنزيليدين سيكلوهكسانون

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الملخص

سلاسل جديدة من الكوبولي استرات العشوائية **V** – **VII** تم تحضيرها عن طريق بلمرة التكثيف بين السطوح لمشتقات ثنائي هيدروكسي بنزيليدين سيكلوهكسانون وثنائي كلوريدات الإيزوفثالويل و/أو التيريفثالويل. تم تأكيد البنية التركيبية بإستخدام التحليل الطيفي بالأشعة تحت الحمراء والتحليل الكمي للعناصر، حيث أظهرت إمتصاص مجموعة الكربونيل الإسترية المميزة. جميع الكوبولي استرات كانت غير قابلة للذوبان في المذيبات العضوية الشائعة، مما يشير إلى وزن جزيئي مرتفع وبنى مرتبة ومنظمة. أظهرت القياسات الكهربائية أن الكوبولي استر **V** و**VII** تصنف كعوازل كهربائية، بينما صنف الكوبولي استر **VI** كشبه موصل. كشف التحليل الحراري أن الكوبولي استر **VI** كان لديه أعلى استقرار حراري ابتدائي (374 °C)، وأن الكوبولي استر **V** له أعلى استقرار نهائي (490 °C)، والكوبولي استر **VII** له أعلى درجة انتقال زجاجي Tg (68 °C) ودرجة انصهار Tm (235 °C)، مع زيادة البلورية من 32% إلى 37%، مما يؤكد أن انتظام البنية الجزيئية يعزز الخصائص الحرارية والبلورية.

معلومات مقالة

الكلمات المفتاحية

كوبوليسترات عشوائية؛
علاقة البنية بالخواص؛
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