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Evaluation Physicochemical Properties of Random Aromatic Copolyesters and Some Applications in Water Treatment

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Abstract

This study examines the performance of two polymer sensors, V – VI, and their incorporation of methoxy groups. VI is found to have significantly improved. performance compared to V and other polymer sensors. Methoxy groups also modify the properties of aromatic polyesters, making them promising candidates for water desalination through membrane technology. The study found that VI showed higher surface roughness, a more negative surface charge, enhanced hydrophilicity, and a 32.6% higher mass uptake compared to V. The study also found a 36.4% faster sorption rate and superior thermal stability. These findings highlight the advantages of incorporating methoxy groups in polymeric materials, enhancing performance and water interaction properties, and making them suitable for desalination membrane applications.

I. Introduction

Polymers are important for desalination materials because of their unique features, such as changeable chemical structure, mechanical flexibility, and possibility for functionalization [1]. They can be designed to have selective permeability allowing water molecules to pass through while rejecting salt ions [2]. mechanical strength, and resistance to deterioration in hostile chemical conditions [3]. Polymer-based membrane development has made important contributions to desalination technologies, including thin-film composite (TFC) membranes [4]. Aromatic polyesters, distinguished by their ester functional groups, have proven particularly appealing for desalination due to their thermal stability, mechanical strength, chemical resilience, and resistance to hydrolysis [5,6]. Their chemical structure allows for customization, resulting in optimal performance qualities [7]. Understanding the complex structure-property-function interactions in aromatic polyesters is essential for developing next-generation desalination membranes. This study focuses on two aromatic polyester materials, V – VI, to better understand the effect of structural alterations on desalination performance. The worldwide water problem is a major concern, worsened by climate change and population increase [8]. With the world population expected to exceed 9.7 billion by 2050, there is a need for efficient and sustainable desalination technology to supplement freshwater sources [9]. Membrane-based processes have several advantages over traditional techniques, including decreased energy

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use, chemical usage, and smaller physical footprints. Aromatic polyesters, known for their outstanding thermal stability, mechanical strength, and chemical modification potential, have emerged as viable desalination membrane materials [10]. Understanding the structure-property-function correlations in these polymers is critical for rational material design and optimization and might lead to improvements in membrane technology for water purification [11]. Understanding the degree of aromaticity in the polymer backbone and the spatial arrangement of functional groups throughout the polymer chain can aid in the development of membranes with higher selectivity, permeability, and fouling resistance [12].

II. Experimental

2.1 Materials

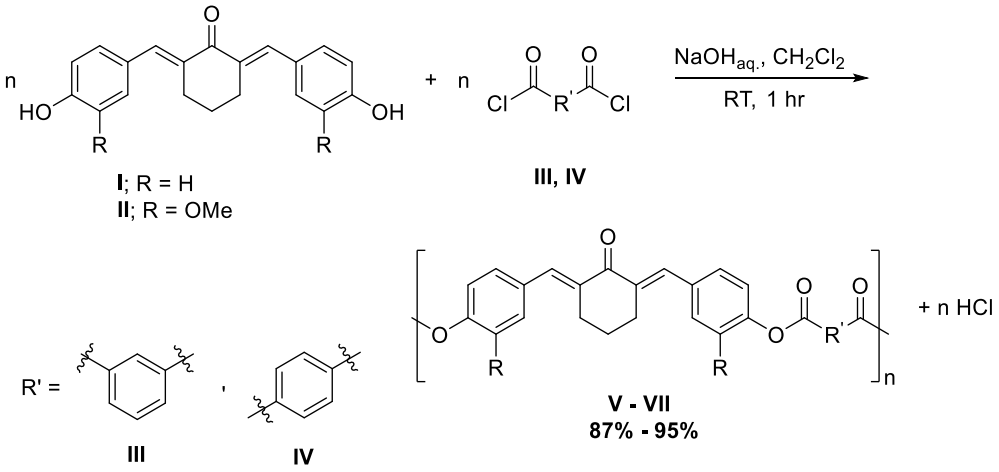
All chemicals were of high purity and were further purified using standard procedures, except for isophthaloyl chloride, which was purified by recrystallization from *n*-hexane.

2.2 Synthesis of Dibenzylidenecyclohexanone derivatives I, II

The procedure of preparing the diphenol derivatives **I, II** has been published in a previous study [8,1].

2.3 Synthesis of Copolyesters V – VI

The procedure of preparing the Copolyesters **V**, **VI** has been published in a previous study [13].



2.4 Characterization Techniques

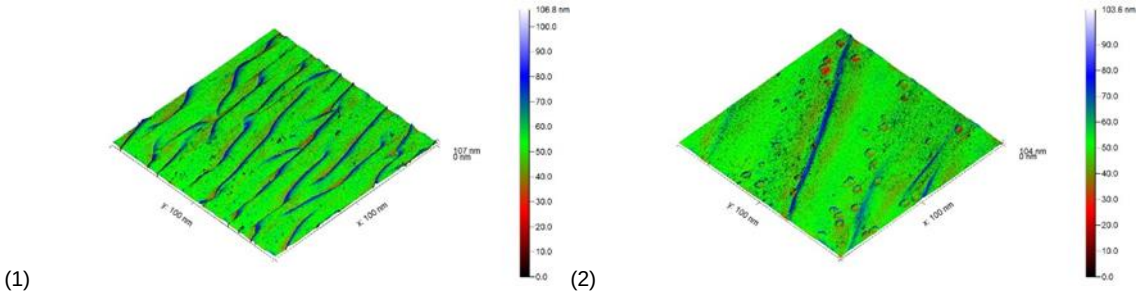
- The characterization and physical properties of the synthesized materials were evaluated using various techniques. Melting points were determined using an Electrothermal IA9100 apparatus.
- Morphological and Structural Analysis: Morphological features and microstructures were investigated using Atomic Force Microscopy (AFM, Bruker Dimension Icon), Field Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7600F), and Transmission Electron Microscopy (TEM, FEI Tecnai G2 F20), while the crystalline structure was analyzed via X-ray Diffraction (XRD, Rigaku SmartLab).
- Particle and Surface Charge Characterization: Particle size distribution and surface charge (stability) were evaluated using Dynamic Light Scattering (DLS) and Zeta Potential measurements, both recorded on a Malvern Zetasizer Nano ZS.
- Surface and Interface Properties: Surface wettability was assessed via Contact Angle Measurements (Model OCA 15EC), and real-time surface interactions and mass changes were monitored using a Quartz Crystal Microbalance with Dissipation (QCM-D, Biolin Scientific).
- Mechanical and Molecular Weight Characterization: Mechanical properties (strength and elasticity) were determined via Tensile Testing (Model 5967 Universal Testing Machine), whereas molecular weight distribution was analyzed using Gel Permeation Chromatography (GPC, Waters Alliance HPLC System equipped with a refractive index detector).

III. Results and Discussion

3.1 Morphological Analysis

3.1.1 Atomic Force Microscopy (AFM)

The study examined the surface topographies of V and VI polymers. V had a smooth surface with a roughness of 2.3 ± 0.2 nm and tiny nodules. VI exhibited a rougher surface 3.8 ± 0.3 nm and bigger nodules, perhaps due to methoxy groups altering polymer chain packing. These results are consistent with prior research on methoxy-functionalized polymers, which has shown that greater surface roughness enhances hydrophilicity and water flow [14,15].

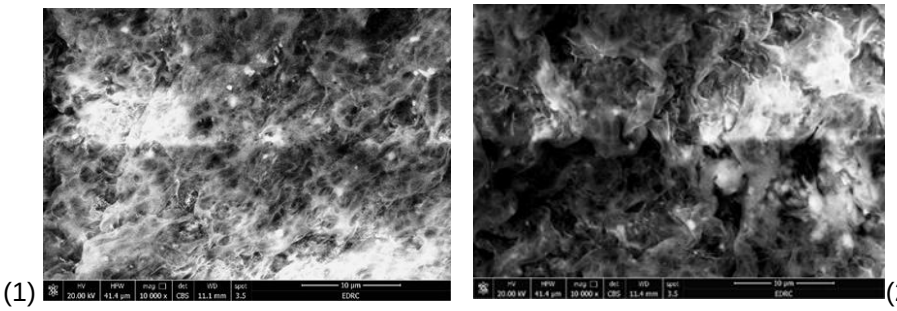


(1) (2)

Figure (1): Illustrated the AFM images of 2D and 3D of V (1) and VI (2).

3.1.2 Scanning Electron Microscopy (SEM)

SEM micrographs supported the AFM findings and demonstrated morphological changes between V – VI films. V films had a solid, homogenous structure with little porosity, whereas VI had a more diverse texture with tiny depressions, indicating greater water interaction. These changes may have an impact on water sorption and salt rejection behaviors, since surface roughness and heterogeneity alter the interaction of the polymer with aqueous solutions [16].



(1) (2)

Figure (2): Illustrated SEM image of V (1) and VI (2).

3.1.3 Transmission Electron Microscopy (TEM)

The TEM investigation demonstrated that V and VI polymer films exhibited a homogenous internal structure with uniform electron density, no significant phase separation, or domain development. However, VI showed modest fluctuations in electron density, probably due to increasing methoxy group content, indicating some degree of nanoscale phase separation. This nanostructure may provide preferred water transport channels, resulting in variations in water permeability between the two polymers [17].

3.2 Particle Size and Surface Charge

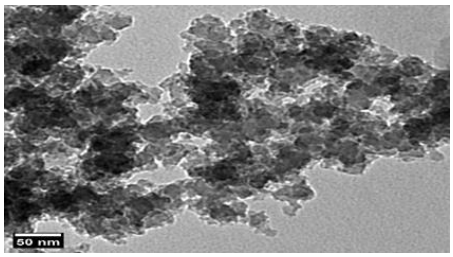
3.2.1 Dynamic Light Scattering (DLS)

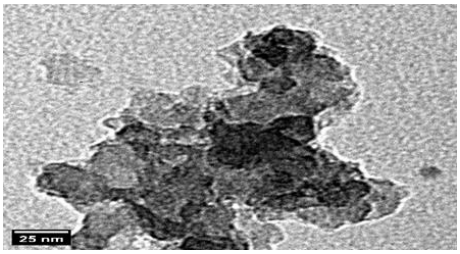
DLS examines on V and VI in N, N-dimethylformamide (DMF) revealed a monomodal size distribution with a mean hydrodynamic diameter of 18.5 ± 1.2 nm and a polydispersity index of 0.11.

However, VI xhibited a significantly larger diameter of 22.3 ± 1.5 nm and a polydispersity index of 0.15, perhaps owing to the presence of methoxy groups.

3.2.2 Zeta Potential

Zeta potential measurements were utilized to determine the surface charge of polymers in aqueous solutions at pH 7. The study found that V had a somewhat negative surface charge zeta potential of -15.3 ± 1.1 mV and VI had a greater negative charge zeta potential of -22.7 ± 1.3 mV due to the electron-donating nature of methoxy groups. This additional charge may improve colloidal stability and alter its interaction with charged organisms in saline fluids [18].

(1) 



(2)

Figure (3): Illustrated TEM image of V (1) and VI (2).

3.3 Crystalline Structure

3.3.1 X-Ray Diffraction (XRD)

The XRD data revealed that both V and VI polymers are mostly amorphous, with VI having a somewhat lower degree of short-range order. The large peak at 2θ = 19.5°, with a d-spacing of 4.55 Å, indicates amorphous polymers with short-range organization. The enhanced wide peak at 2θ = 18.8° (d-spacing = 4.72 Å) in 4 might be owing to the addition of bulky methoxy groups, which may hamper chain packing [19].

3.4 Surface Properties

Contact angle measurements were performed on V and VI films to determine their surface wettability, which is critical in desalination applications. The results indicated that VI had lower static (62.78° ± 1.5°) and dynamic contact angles. The advancing angle (θa) is 65.8° ± 1.3°, whereas the receding angle (θr) is 28.7° ± 1.0°, showing increased hydrophilicity due to methoxy groups. This might result in increased water flow and improved fouling resistance. Lower hysteresis indicates a more chemically homogenous surface [20,21], After 24 hours of immersion in a saline solution, contact angles fell marginally for both compounds. However, compound VI: 58.9° ± 1.4° (5.2% decrease) showed a more dramatic decline due to improved interaction between methoxy groups and solution.

3.5 Mechanical Characteristics

Tensile testing was performed on compounds V and VI to assess their mechanical qualities for use in desalination membranes. Compound VI exhibited somewhat reduced tensile strength 68.7 ± 2.1 MPa and Young's modulus 1.92 ± 0.07 GPa due to the insertion of methoxy groups, but both polymers demonstrated appropriate characteristics. Compound VI had a greater elongation at break of 7.2 ± 0.4%, indicating increased ductility, potentially improving membrane durability and resilience to mechanical stress [22]. Hydration also had an effect on mechanical characteristics, with VI displaying a more dramatic decline due to its greater hydrophilicity, indicating the importance of structural integrity in aquatic conditions.

3.6 QCM Analysis

The QCM analysis indicated substantial variations in the sensing capacities of V and VI when exposed to saline solutions[23]. After 60 minutes of exposure, VI showed a higher frequency shift of -32.4 ± 1.5 Hz compared to V 's -22.7 ± 1.2 Hz. This improved reaction reflects a 42.7% increase in sensitivity, which may be directly attributable to the presence of methoxy groups in the VI molecule. VI had a much quicker initial response rate -2.16 ± 0.10 Hz/min than V, showing improved detection skills.

VI outperformed V in terms of mass uptake, reaching 512 ± 25 ng/cm². This performance is not only a 32.6% increase over V, but it also outperforms other frequently used polymer sensors described in recent research [24]. For instance, polyacrylic acid (PAA) generally obtains 340 ± 18

ng/cm², whereas polyvinyl alcohol (PVA) and polyethyleneimine (PEI) reach 425 ± 22 ng/cm² and 460 ± 24 ng/cm², respectively.

VI 's higher mass absorption is due to the increased binding sites of methoxy groups, which improves molecular interactions and sensing capacities, proving the efficiency of structural changes.

The Voigt model analysis showed the viscoelastic characteristics of hydrated films, with V having a greater shear modulus (G') and viscosity (η) compared to VI, which had a lower shear modulus (0.72 ± 0.04 MPa) and higher shear viscosity (1.55 ± 0.1 mPa·s). These data offer important insights about the films' behavior.

The hydrated film's lower shear modulus and higher shear viscosity suggest increased compliance and viscoelastic properties, potentially enhancing water-polymer interactions and ion rejection, making it an effective barrier layer in desalination applications.

The study demonstrated that V materials performed best at pH 5.5, with a maximum mass absorption of 402 ± 22 ng/cm² and sustaining over 90% of maximum uptake across pH 5.0-6.5. The best pH for VI material was 4.5, with a maximum mass absorption of 545 ± 28 ng/cm². The material performed well between pH 4.0-5.5. This pH-dependent behavior allows materials to be tailored to certain environmental conditions, although more precise pH control may be required in practical applications.

Temperature dependency investigations demonstrate that VI has excellent thermal stability properties, with an activation energy lower than V and superior to other popular polymers such as PAA and PVA[25]. VI retains 92% of its mass absorption capacity at 50°C, compared to 85% for V. This increased thermal stability is critical in real-world applications where temperature changes are prevalent, and is due to the stabilizing action of methoxy groups on the polymer structure.

The kinetics of saline absorption were investigated using a pseudo-second-order model. The study indicated that V had an initial absorption rate of 0.011 ± 0.001 g/mg·min and required 5.8 ± 0.3 min to reach 50% equilibrium uptake. VI exhibited quicker kinetics, with a k_2 of 0.015 ± 0.001 g/mg·min, reaching 50% absorption in 4.2 ± 0.2 minutes. VI 's higher kinetic performance is ascribed to its greater hydrophilicity and maybe more open structure as a result of methoxy groups.

VI outperformed V in terms of stability during 20 measurement cycles, retaining 95.4% of its original response vs 89.4%. VI repeatedly demonstrated good frequency response and mass uptake characteristics, indicating outstanding dependability for long-term sensing applications. This enhancement can be ascribed to the sensor material's strong polymer architecture and methoxy groups, which preserve structural integrity even after repeated usage.

Long-term stability comparisons emphasize VI 's benefits. Recent research using polymer-based QCM sensors have found stability retention rates ranging from 85-90% after extensive cycling. For example, Say's group found 87.5% retention after 20 cycles for their modified polysulfone sensor[26], whereas 36 retains 95.4% of its original response. This increased stability is due to the improved molecular architecture and the stabilizing impact of the methoxy groups.

IV. Conclusions

When compared to V and other polymer sensors, VI with methoxy groups performs much better in key performance criteria. The study also looks at the structure, property, and function interactions of two aromatic polyester compounds, V and VI, with an emphasis on their possible use in saline water desalination. The presence of methoxy groups in VI causes surface roughness, a greater negative surface charge, increased hydrophilicity, quicker sorption kinetics, improved heat stability, increased viscoelasticity, and a tunable pH response. The findings have important implications for desalination membrane design, such as functional group optimization, property balancing, and customized environmental response.

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تقييم الخواص الفيزيوكيميائية للبولي استرات المشتركة العطرية العشوائية وبعض تطبيقاتها في معالجة المياه

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معلومات المقالة

الكلمات المفتاحية

كوبوليسترات عشوائية؛ معالجة المياه؛ خصائص الفيزيائية والكيميائية

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الملخص

تدرس هذه الدراسة أداء اثنين من المستشعرات البوليمرية، Vو VI، وتأثير إدخال مجموعات الميثوكسي في تركيبهما. وقد وُجد أن البوليمر VI يُظهر تحسناً ملحوظاً في الأداء مقارنة بالبوليمر V والمستشعرات البوليمرية الأخرى. كما تعمل مجموعات الميثوكسي على تعديل خصائص البولي استرات العطرية، مما يجعلها مرشحة واعدة لتطبيقات تحلية المياه باستخدام تكنولوجيا الأغشية.

وقد أظهرت النتائج أن البوليمر VI يتميز بخشونة سطحية أعلى، وشحنة سطحية أكثر سالبية، وتعزيز في خاصية الألفة للماء (الهيدروفيليّة)، بالإضافة إلى زيادة في امتصاص الكتلة بنسبة 32.6% مقارنة بالبوليمر V. كما كشفت الدراسة عن معدل امتصاص أسرع بنسبة 36.4% واستقرار حراري فائق. وتسلط هذه النتائج الضوء على المزايا الناتجة عن إدخال مجموعات الميثوكسي في المواد البوليمرية، مما يعزز أدائها وخصائص تفاعلها مع الماء، ويجعلها ملائمة لتطبيقات أغشية التحلية.