

Molecular Conformation and Crystallization Behavior of Bifuran-based Polyesters

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Electronic Supplementary Information

Abstract The utilization of dimethyl 2,2'-bifuran-5,5'-dicarboxylate (BFDCE) as a rigid unit to prepare biomass-derived polyesters has garnered substantial interest, owing to its exceptional thermal stability and excellent mechanical performance. To date, the conformational ordering for crystallization of bifuran-based polyesters is still unclear. Herein, a series of bifuran-based polyesters (PBF_m, where *m*=5–9 represents the number of methylene groups in the aliphatic diols) is synthesized via melt polycondensation using BFDCE and diols. Their crystallization behavior and mechanical performance show a distinct odd-even effect. Despite the restricted chain mobility induced by the rigid bifuran units, the even-numbered PBF6 and PBF8 with a well-defined spherulitic structure exhibit a high crystallinity of 83% and 73%, respectively. In contrast, the odd-numbered PBF5, PBF7, and PBF9 remain amorphous upon melt crystallization. As a result, the crystallized samples show superior tensile strength, while the amorphous counterparts exhibit remarkable ductility. Specifically, PBF6 achieves an exceptional elongation at break of 466% coupled with a tensile strength of 43.7 MPa. These bifuran-based polyesters can serve as sustainable, high-performance alternatives to petroleum-derived polymers, with potential applications in automotive components and other fields requiring tunable material properties.

Keywords Bifuran polyesters; Odd-even effect; Crystallization; Molecular conformation

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INTRODUCTION

Sustainable polymers from renewable biomass have attracted increasing attention in materials science owing to the depletion of fossil resources and severe environmental pollution.^[1–6] The most promising bio-aromatic monomer is 2,5-furandicarboxylic acid (FDCA), which is widely regarded as a pivotal bio-based alternative to terephthalic acid (PTA).^[7–14] For example, compared with traditional petroleum-based poly(ethylene terephthalate) (PET), FDCA-based poly(ethylene furanoate) (PEF) derived from FDCA and ethylene glycol (EG) shows superior gas barrier properties, attributed to the hindered rotation and polar character of the furan ring.^[15–17] In addition, PEF possesses favorable thermal properties, with a glass transition temperature (*T_g*) of 88 °C and a melting point (*T_m*) of approximately 211 °C,

contributing to enhanced heat resistance.^[18] Additionally, PEF exhibits good mechanical performance and comparable thermal stability,^[7,8,19,20] making it a strong candidate for sustainable packaging materials.

Specifically, 2,2'-bifuran-5,5'-dicarboxylic acid (BFDCA), derived from non-food biomass feedstocks including corn cobs and straw,^[1–4,8,10,11,21] is even more intriguing and promising than FDCA. It is an excellent building block for next-generation high-performance bio-based polymers because its conjugated and rigid molecular structure usually brings about strong mechanical properties.^[1–3,11,22] For example, poly(butylene bifuranoate) (PBBf) prepared from dimethyl 2,2'-bifuran-5,5'-dicarboxylate (BFDCE) and 1,4-butanediol (1,4-BD) exhibits a high tensile modulus (2 GPa) and tensile strength (66 MPa), while poly(hexylene bifuranoate) (PHBF) synthesized from BFDCE and 1,6-hexanediol (1,6-HD) shows a high tensile modulus of 1154 MPa and tensile strength of 42.5 MPa.^[23–27] In addition, the bifuran-based polyester poly(ethylene bifuranoate) (PEBF) exhibits UV-blocking ability because of its conjugated bifuran ring system, which shifts the absorption of the polymer into the UV region.^[2] Therefore, the use of

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BFDCA as an alternative monomer for diverse polymers offers an appealing strategy for improving their material properties.

In addition, the rigid and planar bifuran moiety can endow polyesters with crystallization properties different from those of monofuran-based polyesters. This is because the enhanced rigidity potentially perturbs the chain-folding geometries and intermolecular packing,^[28] resulting in distinct crystallization kinetics, anomalous crystallization, and even polymorphism. For monofuran-based polyesters, such as poly(ethylene 2,5-furandicarboxylate) (PEF), the crystallization-induced transition from a low-energy helical conformation to a high-energy zigzag conformation is driven and stabilized by C—H...O hydrogen bonds,^[29] and the higher conformational energy gap gives rise to a crystallization temperature higher than that of PET. Similarly, for the furan-based polyester poly(butylene 2,5-furandicarboxylate) (PBF), studies have shown that strong intermolecular C—H...O=C hydrogen bonds can stabilize the high-energy *syn-syn* conformation, thereby driving crystallization behavior.^[30] This mechanism is analogous to the hydrogen-bonding stabilization of the zigzag conformation in PEF, highlighting the general importance of intermolecular interactions in regulating the crystallization of furan-based polyesters.^[30] However, the molecular-level understanding of the crystallization mechanism of bifuran-based polyesters remains unclear.

In this study, a series of bifuran-based polyesters (PBF m , $m=5-9$) was synthesized *via* melt polycondensation using BFDCE and diols (Scheme 1). This range was selected because it systematically covers both odd and even methylene units to investigate the odd–even effect, while the shorter-chain analogs ($m=2, 4$) are brittle and the longer-chain homologues ($m\geq 10$) would be excessively flexible,^[2,3] rendering the mid-chain series ($m=5-9$) an attractive yet unexplored platform. They show distinct odd–even effects on the crystallization kinetics and morphology. Interestingly, the even-numbered bifuran-based polyesters with a spherulitic crystal structure exhibit rapid crystallization behavior, whereas their

odd-numbered counterparts are amorphous during the melt crystallization process. Notably, the most probable crystal conformations of PBF6 and PBF8 with *trans*^{BFA}–*syn*(–C=O)–*syn*(–C=O) are determined through theoretical and experimental analyses (Scheme 1), and the fiber diffraction pattern reveals that the chain arrangement of PBF8 adopts a zigzag conformation within a triclinic unit cell (space group P1; $a=10.35$ Å, $b=5.50$ Å, $c=18.95$ Å). Specifically, the even-numbered polyester PBF6 shows a high tensile strength (43.7 MPa), while the amorphous odd-numbered PBF9 exhibits a high elongation at break of 547%. This study establishes clear linkages between diol parity and the observed properties, advancing the rational design of bifuran-based polyesters with tunable performance.

EXPERIMENTAL

The experimental details, raw materials, synthesis, and characterization are provided in the electronic supplementary information (ESI).

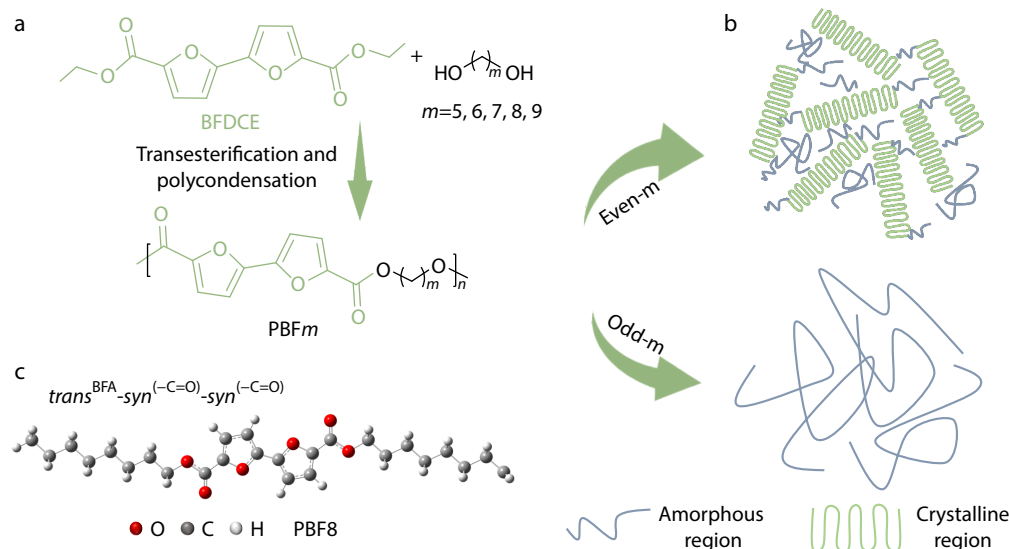
RESULTS AND DISCUSSION

Syntheses of PBF m

The bifuran-based polyesters (PBF m) are synthesized *via* two-stage melt polycondensation comprising transesterification and polycondensation (Scheme S1 and Table S1 in ESI). Their chemical structures are confirmed by ¹H nuclear magnetic resonance (¹H-NMR) (Figs. S1–S5 in ESI) and Fourier-transform infrared (FTIR) spectroscopy (Fig. S6 in ESI). The FTIR spectra reveal the carbonyl stretching vibrations and furan ring deformation modes at 1703–1715 and 1559–1567 cm^{−1} (Table S2 in ESI), respectively. The number-average molecular weight (M_n) ranges from 37600 to 66100 with a narrow polydispersity of approximately 2.00, as estimated by gel permeation chromatography (GPC) analyses (Table S3 in ESI).

Thermal Properties

Thermogravimetric analysis (TGA) is used to determine the ther-



Scheme 1 Schematic illustration of (a) the synthesis route of PBF m , (b) the odd–even effect of the crystallization of PBF m , and (c) the possible conformation in PBF m crystals.

mal stability of bifuran-based polyesters (PBFm). All the polyesters show a 5% weight loss temperature (T_d) of $(365 \pm 4)^\circ\text{C}$ (Fig. 1a and Table 1), consistent with a prior report.^[6] Notably, the T_d value is higher than the about 360°C observed for analogous furan-based polyesters, which is attributed to the superior stability of the bicyclic furan rings.^[31] The glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and corresponding crystallization and melting enthalpies (ΔH_c and ΔH_m) of PBFm are determined using differential scanning calorimetry (DSC) (Figs. 1b, 1c and Table 1). The T_g decreases progressively from 45.6°C to 22.3°C as the alkyl chain length of PBFm increases. As previously reported, the T_g values of poly(ethylene-2,2'-bifuran-5,5'-dicarboxylate) (PBF2) and poly(butylene-2,2'-bifuran-5,5'-dicarboxylate) (PBF4) are 107 and 62°C , respectively.^[2,3] The decrease in T_g is ascribed to the enhanced flexibility imparted by the longer alkyl chains, which facilitates the movement of chain segments.^[31] Comparatively, the T_g values of monofuran-based poly(pentylene furanoate) (PPEf) and poly(hexamethylene furanoate) (PHF) are 15.6 and 23.9°C , respectively.^[27,32] These values are much lower than those of the bifuran-based PBF5 and PBF6.^[31] In other words, the more rigid bifuran-based polyesters exhibit a higher T_g than their monofuran analogs.

Crystallization Behavior

In addition, DSC is employed to study the melting and crystallization processes of PBFm. During the first heating process, all the polyesters exhibited a melting transition. Evidently, the even-numbered bifuran-based polyesters of PBF6 and PBF8 display well-defined crystallization and melting transitions during the first cooling and subsequent second heating scans, but their

odd-numbered counterparts remain amorphous, showing no detectable phase transitions (Figs. 1b–1f). Specifically, PBF6 and PBF8 exhibit endothermic melting peaks at 169 and 157°C during the heating, with corresponding exothermic crystallization peaks appearing at 117 and 112°C during the cooling, respectively (Table 1). The shorter-chain analogs PBF2 and PBF4 have higher melting points of 240 and 215°C , with crystallization temperatures of 169 and 122°C .^[2,3,31] This trend aligns with the known relationship for even-numbered aliphatic-aromatic polyester homologues, where longer alkyl chains lead to lower T_m and T_c values.^[33–36]

Moreover, a pronounced odd-even effect of PBFm is found in the crystalline morphology (Figs. 2a–2e). Odd-even effects are commonly observed in polymeric systems.^[31,33–40] Variations in the aliphatic diol chain length play a key role in determining the thermal properties of polymers. For instance, a series of polyethers (where $n_{\text{CH}_2}=6$ to 12 and 16 denotes the length of the aliphatic chain) is prepared. The odd samples ($n_{\text{CH}_2}=7$ and 9) show higher T_g , T_m , and faster crystallization kinetics than the even samples ($n_{\text{CH}_2}=6, 8$, and 10). Moreover, the unit cells of the even and odd samples are monoclinic and orthorhombic, respectively.^[33] In addition, bio-based long-chain aliphatic polyesters (PnD, where $n=2$ – 10 denotes the carbon number in aliphatic diols) prepared from 1,12-dodecanedioic acid and diols exhibit an odd-even effect. The elongation at break of the odd-numbered series is significantly longer than that of the even-numbered series.^[34] The presence of birefringent Maltese cross patterns is indicative of well-developed spherulites for the even-numbered polyesters of PBF6 and PBF8, confirming their robust crystallization ca-

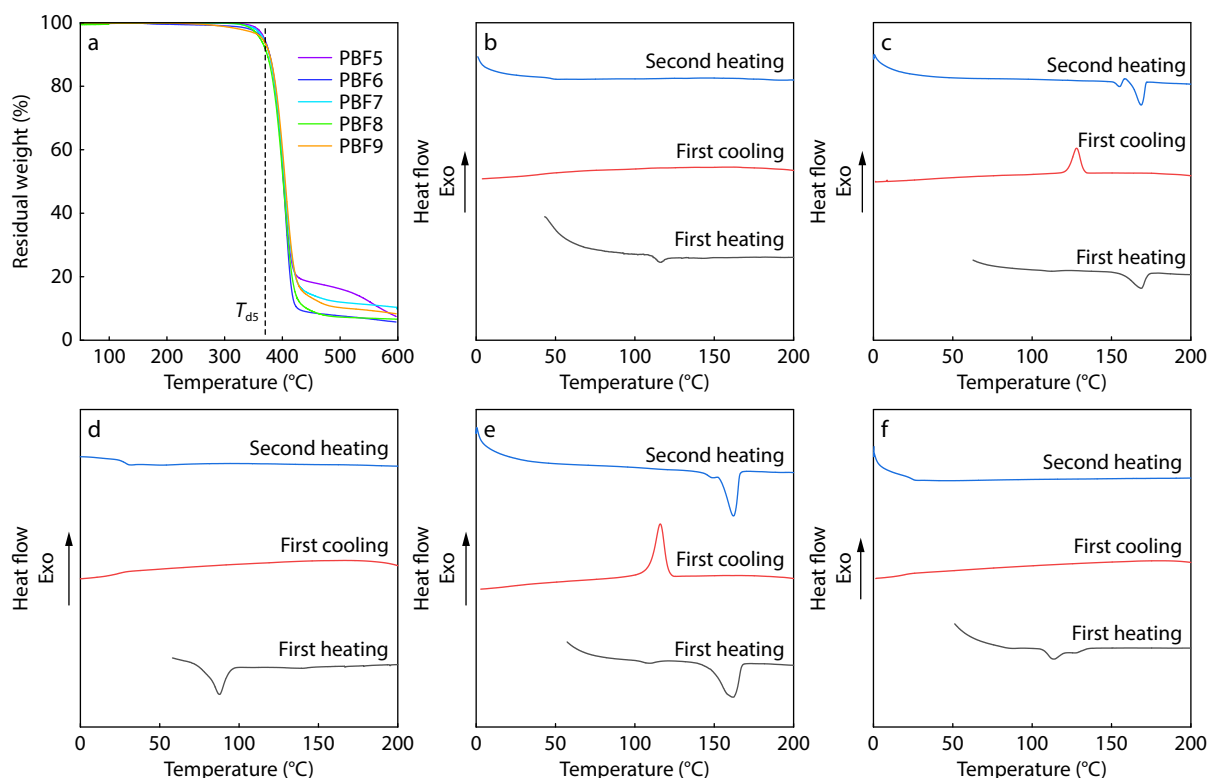


Fig. 1 (a) TGA curves of PBF5, PBF6, PBF7, PBF8, and PBF9 at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere; DSC curves of (b) PBF5, (c) PBF6, (d) PBF7, (e) PBF8, and (f) PBF9 at a heating/cooling rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere.

Table 1 The T_d , T_g , T_c , T_m , ΔH_c and ΔH_m of PBFm ($m=5, 6, 7, 8, 9$).

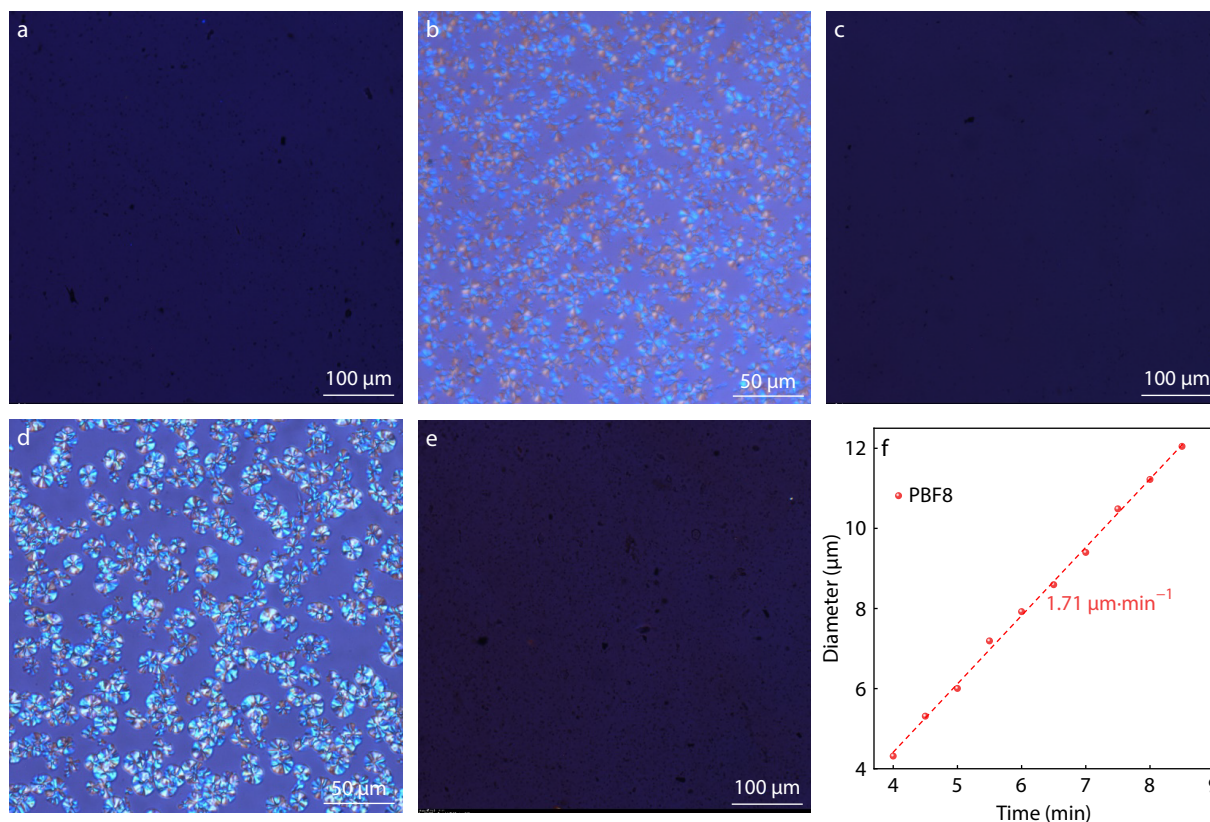
Polyesters	T_d (°C)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_c (J·g ⁻¹)	ΔH_m (J·g ⁻¹)
PBF5	369	45.6	—	—	—	—
PBF6	361	40.2	117	155, 169	42.4	37.7
PBF7	366	28.3	—	—	—	—
PBF8	365	25.5	112	141, 157	53.3	48.6
PBF9	367	22.3	—	—	—	—

capacity. Nevertheless, the odd-numbered polyesters PBF5, PBF7, and PBF9 exhibit optical isotropy consisting of amorphous domains and limited crystallization ability. These morphological observations agree with the DSC analyses, establishing a self-consistent structure-property relationship across experimental techniques. Specifically, the spherulitic growth kinetics of PBF8 quantitatively assessed using temperature-dependent morphological analysis. The onset crystallization temperature ($T_{c, \text{onset}}$) of PBF8, measured by polarized optical microscopy (POM) is 130 °C (Table S4 in ESI), consistent with the non-isothermal DSC results. Subsequent *in situ* observation at these optimized temperatures (Fig. 2f) reveals that the spherulites have an average diameter of about 12 μm , aligning with the value of poly(ethylene 2,5-furandicarboxylate) (PEF) at 11–15 μm .^[41] Growth rate analysis further demonstrates rapid crystallization kinetics, with average velocities reaching 1.71 $\mu\text{m}\cdot\text{min}^{-1}$ for PBF8, confirming the exceptional crystallization capability. Furthermore, the crystallization kinetics of PBF6 and PBF8 are investigated through isothermal DSC analysis (Fig. S7 in ESI). Avrami exponents (n) for PBF6 and PBF8 at 125 °C are determined to be 3.18 and 2.85, re-

spectively. The near-integer n values confirm the predominance of instantaneous nucleation followed by diffusion-controlled growth, which is consistent with the observed spherulitic morphologies.^[14,42,43] It should be noted that the Avrami exponents reported herein were derived from isothermal crystallization experiments conducted at a single temperature (125 °C). A more comprehensive confirmation of the crystallization mechanism would require isothermal analysis across a wider range of temperatures. The odd-even effect can also be observed in the crystallinity of PBFm. The crystallinity (X_c) of the PBFm was calculated using the following equation:

$$X_c = A_c / (A_c + A_a) \quad (1)$$

where A_c and A_a represent the areas of crystalline and amorphous peaks, respectively. Both values can be obtained by fitting the WAXS curves using the Voigt model through nonlinear peak separation calculation in the Jade software. The odd-numbered polyesters PBF5, PBF7, and PBF9 remain amorphous after melt cooling (Fig. 3). The even-numbered polyesters PBF6 and PBF8 exhibit robust crystallinity of 83% and 73%, respectively, under identical conditions, confirming their superior crystallization capability.^[43,44] However, no distinct lamellar reflection is detected in the SAXS profile of PBF6 (Fig. S8 in ESI), suggesting the lack of well-defined long-period lamellar ordering, despite the presence of local crystalline packing revealed by WAXS. This may arise from the weak electron density contrast between the crystalline and amorphous regions, along with a broad and disordered lamellar distribution. The ΔH_c and ΔH_m values for PBF6 and PBF8 closely matched. In contrast, the monofuran-based

**Fig. 2** POM images of (a) PBF5, (b) PBF6, (c) PBF7, (d) PBF8 and (e) PBF9; (f) The spherulite diameter-time trajectories for PBF8 at 130 °C.

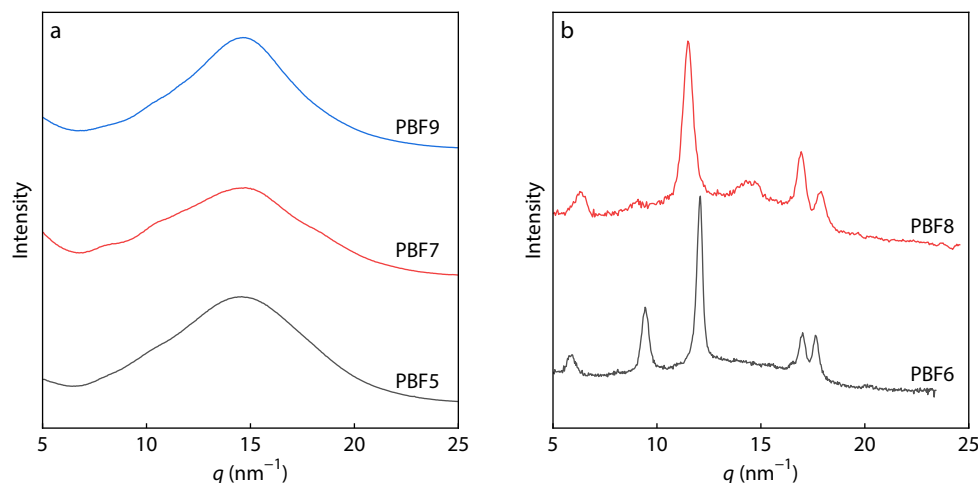


Fig. 3 The WAXS spectra of (a) PBF5, PBF7, and PBF9, (b) PBF6 and PBF8.

poly(hexamethylene furanoate) (PHF) with a lower crystallinity of 49% shows a melting transition but no crystallization transition (Fig. S9 in ESI).^[31] Although the greater molecular rigidity of the bifuran unit can hinder chain mobility and crystallization, it ultimately promotes a higher degree of crystallinity than the monofuran unit, which will be discussed in the following section.

A comparative study is conducted between biphenyl-based polyesters and their bifuran-based analogs. For instance, PBF5 fails to crystallize from melting, whereas its biphenyl counterpart poly(pentamethylene 4,4'-bibenzoate) (PBB5) exhibits measurable crystallization under cooling and a distinct cold crystallization exotherm during heating.^[45] This decreased crystallization ability of PBF5 is attributed to the lower structural symmetry of the furan ring, which disrupts efficient chain packing and nucleation. However, for PBF m with longer even-numbered methylene chains ($m \geq 10$), we anticipate that crystallization will remain at a relatively high level, predominantly governed by alkyl-chain packing.^[46] Furthermore, structurally similar poly(alkylene 4,4'-bibenzoate)s (PBB- n , where $n=5-9$) are typical main-chain liquid crystalline polymers, displaying clear nematic-to-crystalline phase transitions. PBB-5, PBB-7, and PBB-9 form an S_{CA} phase, while PBB-6 and PBB-8 adopt an S_A phase.^[47,48] Contrastively, no obvious liquid crystalline textures are observed in the bifuran-based polyester series. The absence of mesophases in PBF m can be attributed to the reduced symmetry and distinct packing constraints imposed by the bifuran unit, which disrupt the long-range mesogenic ordering necessary for liquid crystallinity. On the other hand, molecular-level insights into this behavior are analyzed. The energy difference between the planar and the 90° twisted conformations is 10.7 and 23.9 kJ·mol⁻¹ for the biphenyl unit and the bifuran unit, respectively (Fig. S10 in ESI). The formation of liquid crystalline phases often requires a balance between molecular rigidity to maintain mesogen alignment, and sufficient flexibility to allow self-assembly into mesophases. This substantially higher rotational energy barrier underscores the greater intrinsic rigidity of the bifuran unit, disrupting the balance. Therefore, bifuran-based polyesters are prone to crystallization or an amorphous state and bypass the liquid crystalline state.

Crystal Structure and Molecular Conformation

Next, we investigate whether crystal structural transitions occur during the melting and cooling of PBF6 and PBF8 (Fig. 4 and Table S4 in ESI). PBF8 exhibits $T_{m, onset}$ and $T_{c, onset}$ at 153 and 137 °C, respectively. Similarly, the $T_{m, onset}$ and $T_{c, onset}$ of PBF6 are 148 and 130 °C (Fig. S11 in ESI), respectively, consistent with the DSC values (Table S4 in ESI). Furthermore, no new scattering peaks or significant peak shifts are observed for PBF6 or PBF8 during heating, indicative of the absence of a crystal structural transition. Therefore, the multiple melting peaks of PBF8 are attributed to variations in the crystal perfection (Fig. 1b). Notably, the peak intensities of PBF8 initially increase during melting (Fig. 4a), revealing an initial enhancement in crystalline order. This behavior aligns with a melting-recrystallization mechanism,^[49] whereby thermal energy facilitates chain realignment before the final melting.

To elucidate the crystallization mechanism of bifuran-based polyesters, the conformational energetics of the PBF6 and PBF8 are estimated using density functional theory (DFT) calculations. This investigation builds upon crystallographic evidence from bifurfuryl acetate (BFAc), in which single-crystal analysis confirms a transparent geometry (*trans*^{BFA}) with coplanar furan rings (dihedral angle=0°).^[25] Such a structural alignment mirrors the extended zigzag conformations in crystalline poly(trimethylene 2,5-furandicarboxylate) (PTF) and poly(ethylene 2,5-furandicarboxylate) (PEF), where the molecular packing efficiency dictates the chain arrangement.^[13,14,29] Based on these structural paradigms, we optimize the six distinct oligomeric conformations of PBF6 and PBF8 (Fig. 5 and Fig. S12 in ESI). Conformer stability assessment based on electronic energy differences reveals the extended *trans*^{BFA}-*anti*(-C=O)-*anti*(-C=O) configuration as the most energetically favorable configuration. Crucially, the energy barrier governing conformational transitions is a critical determinant of crystallization kinetics, proving to be exceptionally low in bifuran systems. Previous studies document a substantial 16 kJ·mol⁻¹ energy penalty for *syn*(-C=O)-*syn*(-C=O) versus *anti*(-C=O)-*anti*(-C=O) conformers in PEF,^[29] whereas our calculations identify only a 0.35 and 0.36 kJ·mol⁻¹ difference between *trans*^{BFA}-*syn*(-C=O)-*syn*(-C=O) and *trans*^{BFA}-*anti*(-C=O)-*anti*(-C=O) arrangements of PBF8 and PBF6, respectively. This minimal energy differential substantiates a crystallization ac-

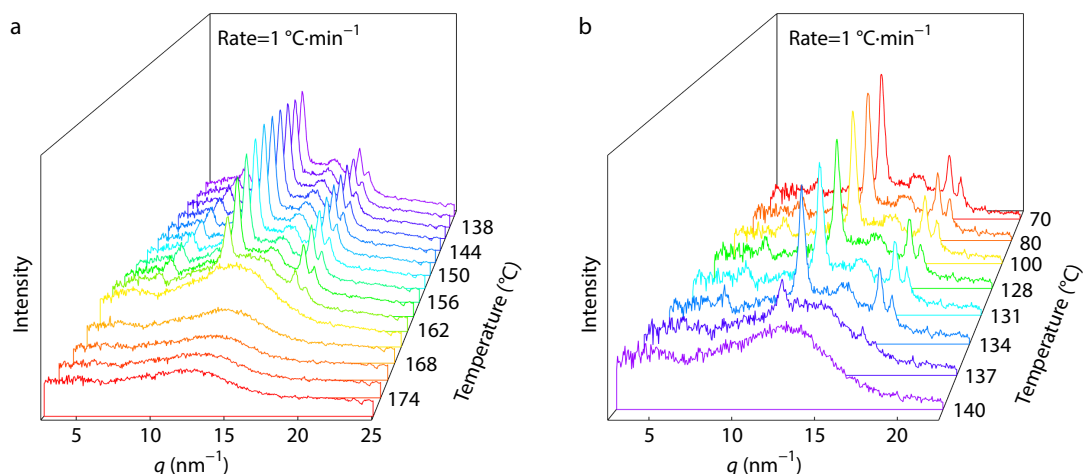


Fig. 4 In situ WAXS spectra of PBF8 during (a) heating and (b) cooling procedures at 1 °C·min⁻¹.

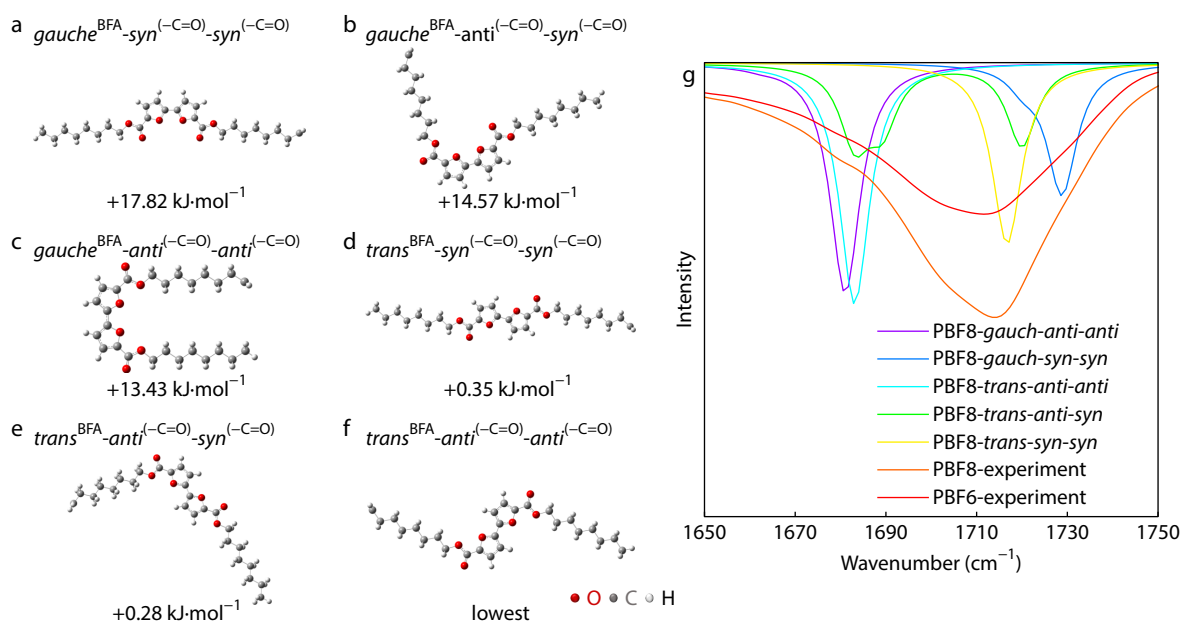


Fig. 5 3D molecular structure of PBF8 possible conformations and their relative stability expressed in terms of electronic energy of (a) *gauche*^{BFA}-*syn*(-C=O)-*syn*(-C=O), (b) *gauche*^{BFA}-*anti*(-C=O)-*syn*(-C=O), (c) *gauche*^{BFA}-*anti*(-C=O)-*anti*(-C=O), (d) *trans*^{BFA}-*syn*(-C=O)-*syn*(-C=O), (e) *trans*^{BFA}-*anti*(-C=O)-*syn*(-C=O), and (f) *trans*^{BFA}-*anti*(-C=O)-*anti*(-C=O), respectively, calculated at the B3LYP/6311+G(d,p) level. *trans*^{BFA} of a *trans*-parallel geometry, *gauche*^{BFA} of a *cis*-parallel geometry; (g) Calculated infrared spectra of PBF8 structural units with various configuration and experiment infrared spectra of PBF6 and PBF8.

celeration of bifuran-based polyesters. The reduced conformational transition barrier facilitates rapid chain reorganization during crystal nucleation and growth, favoring an enhanced crystallizability relative to that of monofuran analogues.

Theoretical IR spectra of PBF8 oligomers reveal that the bifuran conformations including *trans*^{BFA}-*syn*(-C=O)-*syn*(-C=O) (1717 cm⁻¹), *trans*^{BFA}-*anti*(-C=O)-*anti*(-C=O) (1683 cm⁻¹), *gauche*^{BFA}-*syn*(-C=O)-*syn*(-C=O) (1729 cm⁻¹), and *gauche*^{BFA}-*anti*(-C=O)-*anti*(-C=O) (1681 cm⁻¹) exhibit distinct ν (C=O) vibrations. Crucially, the *trans*^{BFA}-*syn*(-C=O)-*syn*(-C=O) conformation (1716 cm⁻¹) aligns with experimental ν (C=O) value at 1714 cm⁻¹ for PBF8 (Fig. 5g). This assignment extends across PBF_m, where the ν (C=O) absorption at 1714 cm⁻¹ confirms the prevalence of *trans*^{BFA}-*syn*(-C=O)-*syn*(-C=O) configuration

in bifuran-based polyesters (Fig. S6 in ESI). Additionally, the *trans*^{BFA}-*anti*(-C=O)-*syn*(-C=O) conformer also shows a reasonable match with the experimental IR spectrum and exhibits a similarly low electronic energy; therefore, it cannot be completely excluded at this stage and requires further confirmation from fiber diffraction analysis. Notably, a slight blue shift of the ν (C=O) band from 1703 cm⁻¹ (PBF5) to 1714 cm⁻¹ (PBF8) is observed (Table S2 in ESI), which is most likely associated with the difference in crystallinity, the highly crystalline even-numbered samples exhibit higher wavenumbers due to stronger intermolecular dipole coupling in the ordered lattice, while the amorphous odd-numbered counterparts show lower values.

This apparent paradox, where the higher-energy *syn*(-C=O)-*syn*(-C=O) conformation dominates despite theoretical prefer-

ence for $\text{anti}^{(-\text{C}=\text{O})}\text{-anti}^{(-\text{C}=\text{O})}$ arrangements, mirrors observations in monofuran systems like PEF and PTF. This phenomenon is attributed to the $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds that preferentially stabilize $\text{syn}^{(-\text{C}=\text{O})}\text{-syn}^{(-\text{C}=\text{O})}$ conformers.^[13,30] However, the exceptionally narrow energy gap between $\text{syn}^{(-\text{C}=\text{O})}\text{-syn}^{(-\text{C}=\text{O})}$ and $\text{anti}^{(-\text{C}=\text{O})}\text{-anti}^{(-\text{C}=\text{O})}$ configurations in bifuran-based polyesters ($0.35\text{ kJ}\cdot\text{mol}^{-1}$) introduces ambiguity regarding the role of hydrogen bonding.

To validate the potential $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding in bifuran polyesters, the crystal structure of PBF8 via fiber diffraction is resolved (Fig. 6a). The fiber diffraction refinement of PBF8 yielded an R-factor of 0.75 (Fig. S13 in ESI). Analysis of independent reflections from oriented films establishes a triclinic unit cell (space group P1) with parameters $a=10.35\text{ \AA}$, $b=5.50\text{ \AA}$, c (fiber axis) $=18.95\text{ \AA}$, $\alpha=95.5^\circ$, $\beta=93.5^\circ$, $\gamma=93.3^\circ$ (Table S5 in ESI). The unit cell accommodates two antiparallel chains, and each unit cell contains one PBF8 repeat unit. Structural modeling reveals strict coplanarity of the difuranyl moiety (dihedral angle $<5^\circ$) coupled with all-*trans* zigzag methylene conformations (Fig. 6b). The alkyl chains are oriented out-of-plane relative to the bifuran ring and form a zigzag-shaped geometry together with the bifuran ring along the c -axis. Critically, interatomic distances preclude significant hydrogen bonding: furan ring planes are separated by $4.44\text{ \AA}$, and the distances of $\text{C}-\text{H}\cdots\text{O}=\text{C}$ and $\text{C}-\text{H}\cdots\text{O}$ (furan ring) are 3.15 and $3.95\text{ \AA}$, respectively. No significant hydrogen bonding interactions are identified in the crystal structure.^[13,29] Notably, the $\text{syn}^{(-\text{C}=\text{O})}\text{-syn}^{(-\text{C}=\text{O})}$ conformation observed in the crystal is not the lowest energy conformer according to DFT calculations because DFT represents isolated chains, whereas crystal packing involves a balance between conformational and packing energy. The zigzag geometry of $\text{syn}^{(-\text{C}=\text{O})}\text{-syn}^{(-\text{C}=\text{O})}$ enables tighter chain packing in the triclinic unit cell, similar to that observed in the PEF and PTF systems.^[13,30] The absence of strong intermolecular interactions suggests that the low conformational transition barrier ($0.35\text{ kJ}\cdot\text{mol}^{-1}$) as the primary driver of rapid crystallization in PBF8. Unfortunately, the high glass transition temperature and chain rigidity of PBF6 currently pose a challenge for the preparation of oriented fibers.

Mechanical Properties

Finally, the mechanical properties of PBF m are studied (Fig. S14

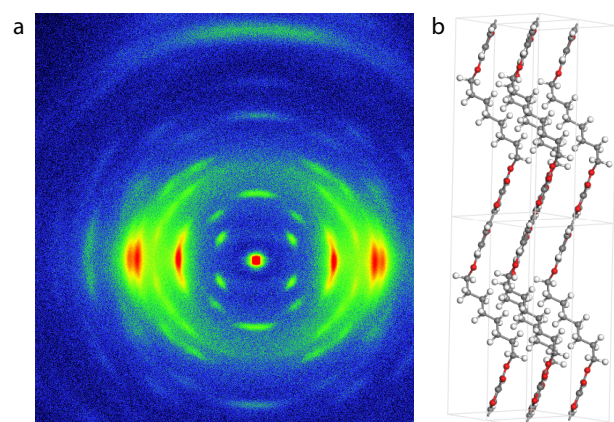


Fig. 6 (a) 2D WAXS pattern and (b) scheme of the crystal structure of PBF8 fiber.

in ESI). Dumbbell-shaped tensile specimens (2 mm in width at the narrow section, 0.1 mm thickness) are prepared by melt pressing followed by quenching at $30\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ (see ESI for details). Tensile tests are performed at a crosshead speed of $0.05\text{ mm}\cdot\text{s}^{-1}$ with a gauge length of 7 mm (strain rate $\approx 0.007\text{ s}^{-1}$), and all samples are tested in the as-quenched state without further annealing. A significant difference in tensile modulus and yield strength is observed between the even- and odd-numbered bifuran polyesters. The even-numbered polyesters PBF6 and PBF8 have high tensile moduli of 1159 and 773 MPa and yield strengths of 20.1 and 22.1 MPa, respectively. However, the odd-numbered PBF7 and PBF9 exhibit markedly lower moduli of 364 and 398 MPa and yield strengths of 12.1 and 11.8 MPa, respectively. This distinct mechanical behavior arises from the differences in crystalline structures (Table S6 in ESI). Interestingly, PBF6 exhibits not only a high tensile strength (43.7 MPa), but also an elongation at break of 466%, making its overall mechanical performance competitive with that of PET, particularly in terms of ductility. This seemingly counterintuitive behavior of high crystallinity accompanied by high ductility, attributing to a combination of factors, including the molecular weight, methylene chain length, and crystallinity, rather than to any single structural parameter.^[50,51] Such unprecedented mechanical performance makes bifuran-based polymers potent candidates for biaxial stretching processes in next-generation high-performance materials.

CONCLUSIONS

In summary, we demonstrate that the alkyl chain acts as a molecular switch that governing the crystallization and mechanical properties of PBF m . The even-numbered polyesters exhibit high crystallinity and form well-defined spherulites, whereas their odd-numbered counterparts remain amorphous. DFT calculations reveal an ultra-low conformational energy barrier of 0.36 and 0.35 for PBF6 and PBF8, respectively, which accounts for the rapid chain alignment during crystallization and the superior crystallization capability. Fiber diffraction confirms a triclinic unit cell (space group P1; $a=10.35\text{ \AA}$, $b=5.50\text{ \AA}$, $c=18.95\text{ \AA}$) with zigzag chain conformations. Notably, the even-numbered polyester PBF6 shows a high tensile strength (43.7 MPa), while the amorphous odd-numbered PBF9 exhibits a high elongation at break of 547%. These bifuran-based polyesters are clearly superior to monofuran analogues and conventional petroleum-based polymers, offering a sustainable platform for tunable high-performance materials.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3824-1>.

Data Availability Statement

The data that support the findings of this study are available upon request from the corresponding authors.

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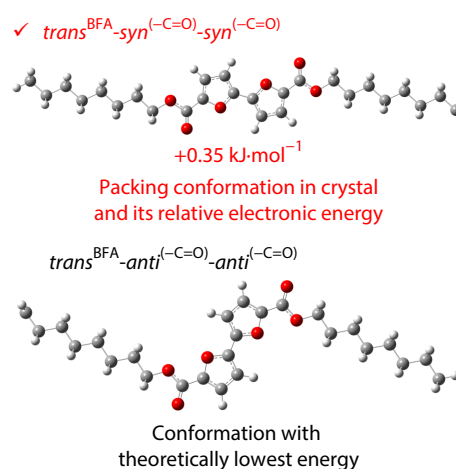
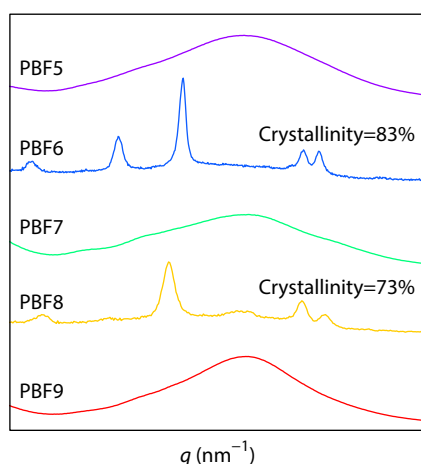
Graphical Abstract

Molecular Conformation and Crystallization Behavior of Bifuran-based Polyesters

Wen-Ting Li, Le Shen, Guang-Jian Liao, Hai Wang, Bi-Jin Xiong, Guo-Chuan Yin, Yong-Gui Liao, Jin-Tao Zhu, and Xiao-Lin Xie

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The rigid bifuran unit directs conformational ordering during melt crystallization, yielding exceptional crystallinity up to 83% in even-methylene polyesters PBF6 and PBF8.



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