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Synthesis and characterization of bio-based amorphous polyamide from dimethyl furan-2,5-dicarboxylate

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Abstract: In this research, bio-based polyamide (bio-PA) was synthesized from dimethyl furan-2,5-dicarboxylate and 1,3-cyclohexanedimethanamine by melt polymerization. The properties of bio-PA were analyzed by Fourier transform infrared spectrometer (FTIR), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and thermal gravimetric analysis (TGA), respectively. The results show that this bio-PA presents high glass transition temperature (T_g) from 150°C to 180°C and poor crystallization due to the asymmetric rigid structure of cyclohexane and furan. Its molecular weight is low, ascribing to the large steric hindrance from cyclohexane and furan, and the side reaction of N-methylation and decarboxylation. Besides, the results of solubility reveal that this bio-PA can be dissolved in DMSO, DMF and DMAC.

Keywords: bio-based polyamide, furan polymer, dimethyl furan-2,5-dicarboxylate, 1,3-cyclohexanedimethanamine, melt polymerization

Introduction

Polyamide (PA) has good comprehensive properties, including mechanical properties, heat resistance, wear resistance, chemical resistance and easy processing, is widely used as one of engineering plastics. It is usually synthesized by polycondensation of diamine and diacid [1], diamine and diacid derivatives or ring-opening polymerization of lactam [2,3]. At present, the monomer of polyamide, such as terephthalic acid, isophthalic acid, hexamethylene diamine and butane diamine, is mainly derived from petroleum resources, which are non-renewable and cause energy crisis. Nowadays, utilization of biomass to develop bio-based polyamide attracts many researchers attention and becomes a new hotspots [4].

Furandicarboxylic acid (FDCA) is a kind of bio-based commercial compound, is usually generated from 5-(hydroxymethyl)furfural (5-HMF) by chemical [5-8] or biological method [9]. HMF is mainly derived from natural hexose (glucose, monosaccharide) [10]. The carbon content of FDCA is same as hexose and there is no carbon release during the conversion. Therefore, FDCA has been regarded as one of the 12 most valuable bio-based platform compounds by US Department of Energy, can be used to synthesize the furanyl polyester and polyamide. Compared FDCA with terephthalic acid (TPA), their physicochemical properties are similar. The carbon atom of furan is less than that of benzene and its aromaticity is weak, the bond angle is small and the rigidity is strong. This leads to the FDCA-based polymers possess better thermodynamic and mechanical properties than that of phthalic acid polymers. At present, the research on furandicarboxylic acid has been greatly developed. For example, FDCA has been applied to synthesize the semicrystalline aromatic polyesters, poly(ethylene 2,5-furandicarboxylate) (PEF) [11] and poly(butylene 2,5-furandicarboxylate) (PBF) [12,13]. The results show that polyesters based on FDCA exhibits lower T_m and higher T_g than that of polyesters from TPA, which makes it a potential substitute for petroleum-based polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [14]. Correspondingly, the FDCA-based polyamides as a substitute of traditional aromatic polyamides also attract widespread attention.

As early as 1961, Hopff and Krieger [15] firstly reported the synthesis of bio-based polyamide with furan ring, which broke the dependence of polyamide industry on petroleum resources. Afterwards, Fehrenbacher [16] synthesized poly(hexamethylene furanamide) (PA6F), poly(octamethylene furanamide) (PA8F), poly(decamethylene furanamide) (PA10F), and poly(dodecamethylene furanamide) (PA12F) via melt polycondensation using organometallic catalysts. Yohana [17] synthesized copolyamide of poly(butylene-2,5-furan dicarboxylamide) (PA4F) and poly(butylene adipamide) (PA46) through consecutive prepolymerization and solid-state polymerization. Recently, transparent PA attracted many researchers attention and exhibited potential application in many fields, such as machine parts, optical instruments and sports equipment. However, there are few literatures on the preparation of transparent PA, especially transparent bio-based PA. Transparency is closely associated with crystallinity. Therefore, it is important to develop bio-based amorphous polyamide. Thibault [18] synthesized a series of polyamides and copolyamides by melt polycondensation from FDCA, isophthalic acid (IPA) and 1,6-hexanediamine. It is observed that the polyamides synthesized from dicarboxylic acid or its derivatives present low crystallinity or amorphous structure, the copolyamides exhibit low melting point and crystallinity with the increase of FDCA content [19-22]. Wilsens [23] investigated the depression effect of furan rings on the formation of hydrogen bonds among amide groups using small molecule compounds. It found that the oxygen heteroatom in FDCA ring acts as a hydrogen bond acceptor to form intramolecular hydrogen bonds, which reduce the formation of intermolecular hydrogen bonds and interaction forces. This is benefit to prepare the amorphous and transparent PA materials. Besides, 1,3-cyclohexanedimethanamine is a mixture of cis-trans isomer, which destroys the regular structure of polymers and guarantees the high transparency. Its cyclohexane structure is benefit to the high glass-transition temperature.

In this research, bio-based amorphous polyamide was designed and synthesized by melt polymerization from dimethyl furan-2,5-dicarboxylate and 1,3-cyclohexanedimethanamine. The effect of reaction temperature and time on the properties of target product was fully investigated.

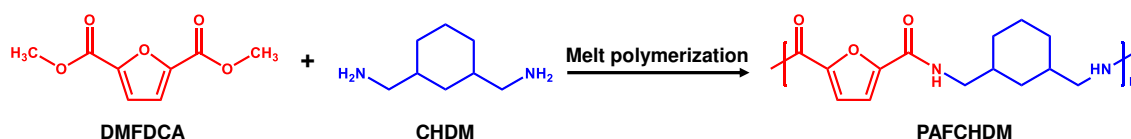
Experimental section

Materials

Dimethyl furan-2,5-dicarboxylate (DMFDCA, 98%), 1,3-cyclohexanedimethanamine (Isomer mixture, CHDM, 99%) was purchased from Tokyo Chemical Industry. Dimethyl sulfoxide-d₆ (DMSO) was purchased from Shanghai Yien Chemical Technology Co. Ltd. Sulfuric acid (H₂SO₄, 98%) was purchased from Pinghu Chemical Reagent Factory.

Synthesis of polyamide

5.0g (27.1mmol) DMFDCA and 3.86g (27.1mmol) 1,3-cyclohexanedimethanamine were transferred to a glass tube and gradually raised to 120°C, maintaining for 0.5h under the protection of nitrogen. Then, the prepolymer was further heated to 230°C, 240°C, 250°C and reacted some hours. The pressure was controlled below 300Pa. Finally, pale yellow transparent polyamide PAFCHDM was obtained, its chemical equation is shown in Scheme 1.



Scheme 1. The equation for synthesis of furan polyamide in this research. DMFDCA refers to dimethyl furan-2,5-dicarboxylate and CHDM refers to 1,3-cyclohexanedimethanamine.

Measurements

For infrared spectra testing, the polymers were ground into powder and carried out on Fourier transform infrared spectrometer (FT-IR) with attenuated total reflectance (ATR) method.

¹H and ¹³C NMR spectra were recorded on a Bruker 600 MHz NMR spectrometer at room temperature. All the compounds were dissolved in dimethyl sulfoxide-d₆ (DMSO-d₆). The spectra were internally referenced to tetramethylsilane (TMS). About 10mg and 50mg sample were dissolved in 5mL solvent using for ¹H NMR and ¹³C NMR testing, respectively. 108 scans were recorded for ¹H NMR and 1280 scans for ¹³C NMR.

The thermal behavior of polymers was examined by differential scanning calorimetry (DSC). The thermograms were obtained from 5mg to 10mg samples at heating and cooling rates of 20°C/min from 30°C to 250°C under a nitrogen flow of 20mL/min.

Thermogravimetric analysis (TGA) was performed on TGA 209F1 from 50°C to 600°C under nitrogen flow of 20mL/min at a heating rate of 10°C/min.

XRD patterns were recorded on Rigaku D/max-2550 using Cu K α radiation in the scan range from 5° to 90° with increment of 0.02.

For intrinsic viscosity measurement, the samples were dissolved in 98% sulfuric acid to get solutions of 0.5g/dL and measured with JWC-32C viscometer in 25 \pm 0.02°C water bath. The flow time of solution and sulfuric acid were recorded as t and t_0 , respectively. The relative viscosity (η_r) and specific diversity (η_{sp}) were calculated as follows:

$$\eta_r = \frac{t}{t_0} \quad (1)$$

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

The solution concentration was marked as C . The intrinsic viscosity $[\eta]$ can be calculated by one-point method (Solomon and Ciuta relationship)[24] as follows:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{C} \quad (3)$$

Finally, the viscosity-average molecular weight (M_v) was calculated according to the following equation [25]:

$$[\eta] = 5.43 \times 10^{-4} M_v^{0.73} \quad (4)$$

As comparison, Weight-average Molecular Weight (M_w) was measured by Shimadzu Gel Permeation Chromatography CTO-20A (GPC-20A). All the PA samples were dissolved in DMF and polystyrene was used as standard.

Results and discussion

Structure analysis of furan polyamide

Figure 1 presents the FT-IR spectra of synthesized furan polyamides. The C=C stretching vibrations ($1560\text{--}1580\text{cm}^{-1}$), C-O-C groups (1011cm^{-1}), and the out-of-plane deformed vibrations of C-H groups (967cm^{-1} , 820cm^{-1} , and 755cm^{-1}), can be found in all the PAFCHDM samples, demonstrating the introduction of furan rings in these polymers. The peak at 1720cm^{-1} was observed for the 120-230-60min sample, which corresponds to the free C=O from COOCH_3 and demonstrates the DMFDCA was not fully reacted at 230°C . When the temperature increases to 240°C , the peak disappeared, indicating the full conversion of ester to amide groups. The two peaks at 3430cm^{-1} and 3294cm^{-1} are attributed to the stretching vibrations of “free” and hydrogen bonded N-H in amide groups, suggesting the presence of hydrogen bonds in these polyamides. The formation of amide groups is also confirmed by the presence of amide I, II and III complex vibration bands, which is located around 1652cm^{-1} , 1530cm^{-1} and 1292cm^{-1} , respectively.

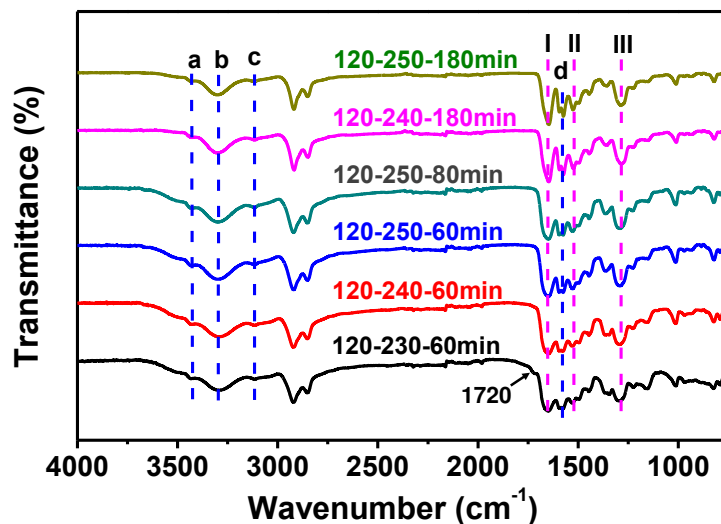


Figure 1. FT-IR spectra of PAFCHDM. (a) stretching vibration of free N-H; (b) stretching vibrations of hydrogen-bonded N-H groups; (c) C-H of furan stretching; (d) C=C stretching vibrations.

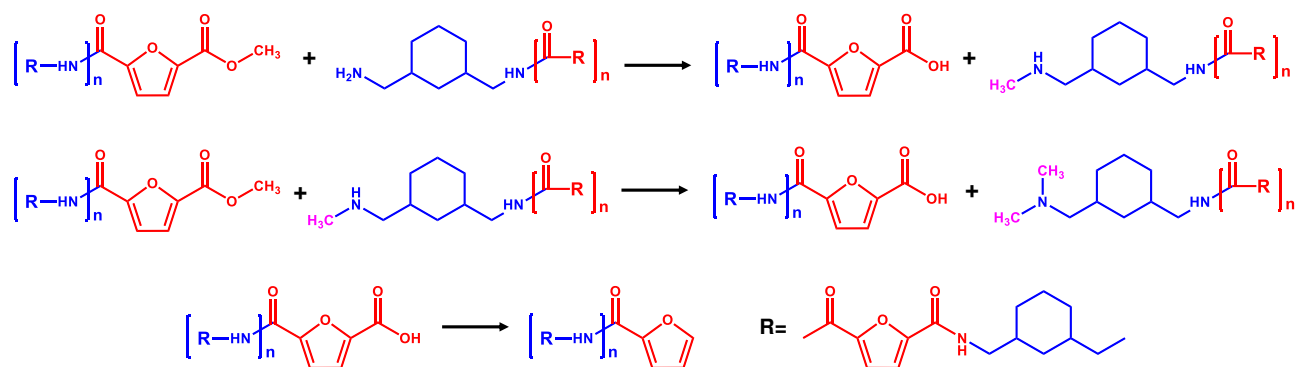


Figure 2. N-methylation and decarboxylation side reaction during the melt polymerization from DMFDCA and CHDM.

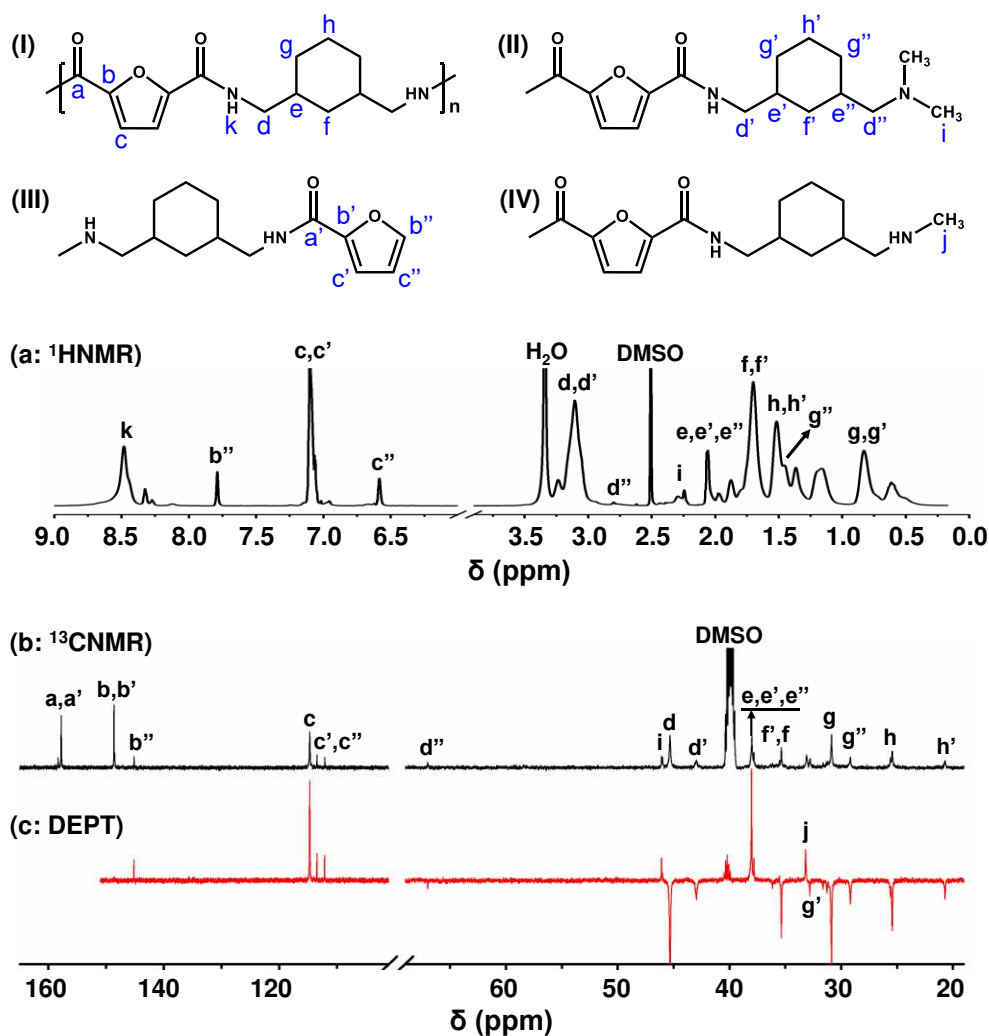


Figure 3. (a) ^1H NMR of the synthesized PAFCHDM, including three possible byproducts; (b) ^{13}C NMR of PAFCHDM, which was dissolved in DMSO- d_6 ; (c) DEPT spectrum of the PAFCHDM, DEPT spectroscopy is a type of carbon spectroscopy, is used to distinguish the primary carbon, secondary carbon, tertiary carbon and quaternary carbon.

Figure 2, 3 presents the possible reaction and NMR results of products, respectively. As shown in Figure 3(a), the proton signals at 7.1ppm is assigned to c and c' of furan rings. The resonances at 8.5ppm attribute to the proton k of amide bonds. The proton signal peaks at 6.6ppm and 7.8ppm are presumed to the hydrogen on c" and b". The signal peak at 2.25ppm may be ascribed to the proton hydrogen of i after N-methylation reaction. From this result, it can be inferred that the N-methylation and decarboxylation occur during the polymerization. This leads to the low molecular weight of PAFCHDM and will be further explained by ^{13}C NMR spectrum.

Figure 3(b, c) exhibits the ^{13}C NMR and DEPT spectra of PAFCHDM. DEPT spectroscopy is a type of carbon spectroscopy, is mainly used to distinguish the primary carbon (CH_3), secondary carbon (CH_2), tertiary carbon (CH) and quaternary carbon (C). The peaks of CH and CH_3 are upward, which of CH_2 is downward, and no peak appears for the quaternary carbon in DEPT spectrum. In this research, the resonance peaks d, d', d" are methylene signals, and the d', d" are ascribed to the N-methylation reaction between DMFDCA and CHDM [27, 28]. The resonance peaks b, b', b" and c, c', c" are attributed to the carbon atom on furan ring. The peaks b', b" and c', c" are methine signals derived from the byproduct of decarboxylation. Peaks i and j are attributed to the signal of $-\text{CH}_3$ after the single and double substitution of NH_2 . The N-methylation and decarboxylation blocks the terminal amino group and the steric hindrance increases, leads to the termination of reaction or the reduction of reaction activity, resulting in the low molecular weight of PAFCHDM.

Thermal properties and crystallization

The bio-PA PAFCHDM was synthesized according to Scheme 1, their molecular weight was measured by one-point method [24] and all the results are listed in Table 1. It shows that the M_v of PAFCHDM under different conditions is low and almost the same, hasn't obvious change with the

temperature and time. That is because 1,3-cyclohexane dimethyl-amine contains a rigid cyclohexane, which is a mixture of cis- and trans-isomers. This leads to the high steric hindrance and makes the movement of diamines difficult. At the same time, Wilsens [26] demonstrated that FDCA requires more energy to become activity than regular phenyl based monomers. DMFDCA is a derivative of FDCA, is rigid and hard to move. This cause the reaction activity between DMFDCA and 1,3-cyclohexanedimethanamine is poor, resulting in the low molecular weight. Most important, N-methylation and decarboxylation is another reason for the low molecular weight of PAFCHDM, as shown in Figure 2.

Table 1. The relative viscosity (η_r), viscosity-average molecular weight (M_v), glass transition temperature (T_g), temperature at 5% weight loss ($T_{d-5\%}$) and the temperature at maximum weight loss rate (T_{d-max}) of PAFCHDM synthesized under different conditions.

Sample code	Temperature (°C)	Time (min)	Yield (%)	T_g (°C)	$T_{d-5\%}$ (°C)	T_{d-max} (°C)	η_r	M_v (g/mol)	M_w (g/mol)
PA-1	120/230	30/60	--	181.2	286	412	1.061	1621	2848
PA-2	120/240	30/60	98.5	177.7	289	410	1.063	1692	3359
PA-3	120/250	30/60	95.5	167.0	311	411	1.066	1799	3940
PA-4	120/250	30/80	95.9	161.0	314	409	1.068	1873	4242
PA-5	120/240	30/180	96.0	163.7	344	436	1.075	2136	5096
PA-6	120/250	30/180	96.0	155.9	391	436	1.096	2777	6545

Note: -- indicates the incomplete reaction

Thermal properties and crystallization of the PAFCHDM were analyzed by DSC, XRD and TGA respectively, all the data are summarized in Table 1. Figure 4 presents the DSC and XRD results of selected PAFCHDM samples. As shown in Figure 4a, it shows that PAFCHDM exhibits a high T_g of 150°C to 180°C, which is mainly attributed to the rigid structure of furan ring and 1,3-cyclohexanedimethanamine. The T_g value decreases with temperature and time increase. This is

different from the general polymerization process. It is inferred that the oligomer cyclization occurs during the polymerization process [29]. At the beginning, ring-like polyamide is rigid and the movement of molecular chains is difficult, which leads to a high T_g . As the reaction continuous, the ring-like molecular chain becomes long and mobility, which leads to the decrease of T_g . In addition, there are no melting endothermic peaks and crystallization peaks in the second heating curve, which proves the amorphous characterization of PAFCHDM. It is mainly because 1,3-cyclohexanedimethanamine (cis-trans isomer mixture) contains a cyclohexane structure, which includes a ship-type and chair-type conformation, destroys the crystallinity. Moreover, the furan ring inhibits the formation of intermolecular hydrogen bonds and reduces the crystallinity in some extent. Figure 4b shows the XRD spectrum of PAFCHDM under different post polymerization temperature. All samples exhibit a similar profile and present a wide diffraction peak around 19° . This indicates that PAFCHDM is difficulty to crystallize and the crystallinity is low, which is benefit to its transparent.

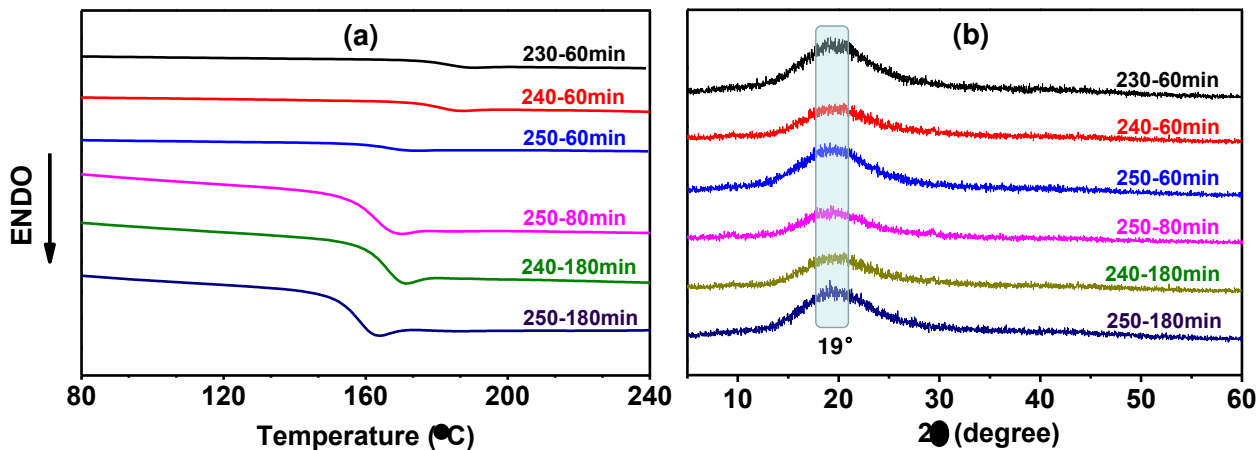


Figure 4. (a): Second heating curves of PAFCHDM from 80°C to 240°C under nitrogen; (b): XRD profiles of all the PAFCHDM samples.

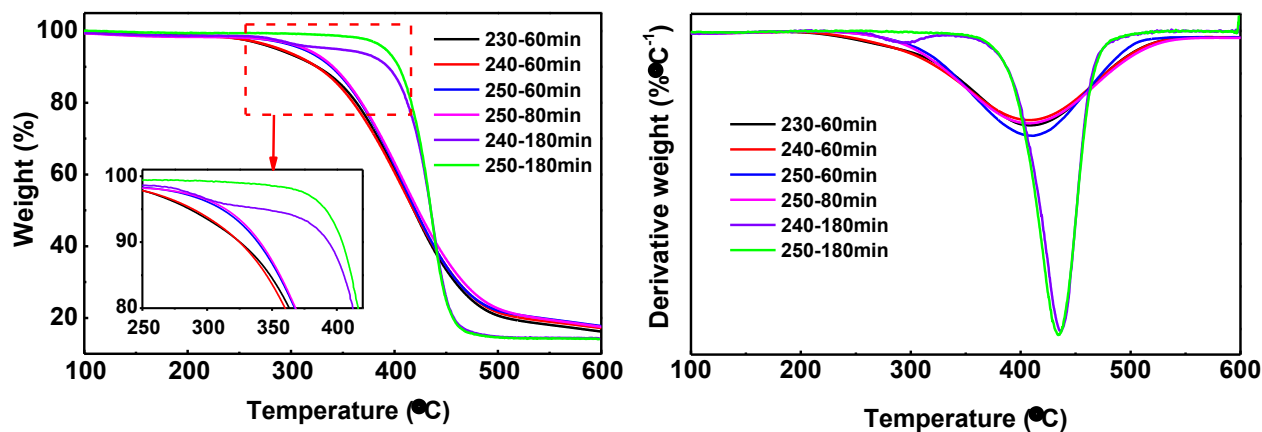


Figure 5. TGA (a) and DTG (b) curves of PAFCHDM, which is recorded from 100°C to 600°C under nitrogen.

The thermogravimetric traces were recorded at the range of 100-600°C under nitrogen atmosphere, the results are shown in Figure 5. It indicates that PAFCHDM starts to decompose around 286-314°C and possesses a T_{d-max} above 400°C, confirming the good thermal stability. With the temperature increases, the $T_{d-5\%}$ increases and the T_{d-max} has no obvious change. That is because the molecular weight of synthesized PAFCHDM has not significant improvement.

Solubility of furan polyamide

Application of high-performance polymers is often limited by their poor solubility in organic solvents. Therefore, the solubility of PAFCHDM in several solvents was studied. The results are listed in Table 2. It shows that the PAFCHDM can be dissolved in polar aprotic solvents at room temperature, such as DMSO, DMF, DMAC and NMP. The main reason for its good solubility is ascribed to the low molecular weight and amorphous structure, which makes the solvent easy to spread in molecular chains. Additionally, the inhibitory effect of furan ring reduces the hydrogen bond and intermolecular force, improving the solubility.

Table 2 Solubility of furan polyamides in various solvents

Sample	DMSO	DMF	DMAC	THF	CHCl ₃	Methanol	Acetone	NMP
PAFCHDM	++	++	++	-	-	+	-	++

Note: ++ soluble at room temperature; + soluble under the addition of LiCl and heating; - insoluble under the addition of LiCl and heating.

Conclusions

The bio-based furan polyamide PAFCHDM was synthesized by melt polymerization from dimethyl furan-2,5-dicarboxylate and 1,3-cyclohexanedimethanamine. ¹H NMR and ¹³C NMR demonstrate the successful synthesis of polyamide and the polymerization process is prone to N-methylation and decarboxylation, which leads to the low molecular weight of synthesized PAFCHDM. The results of DSC and XRD show that the furan ring and asymmetric 1,3-cyclohexanedimethanamine inhibits the crystallization, which has an important effect on the polymer crystallinity. It was also found that the PAFCHDM could be dissolved in DMSO, DMF, DMAC and NMP at room temperature.

Declaration of competing Interest

The authors declare that they have no known competing financial interests to influence the work reported in this research.

Acknowledgement

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Figures

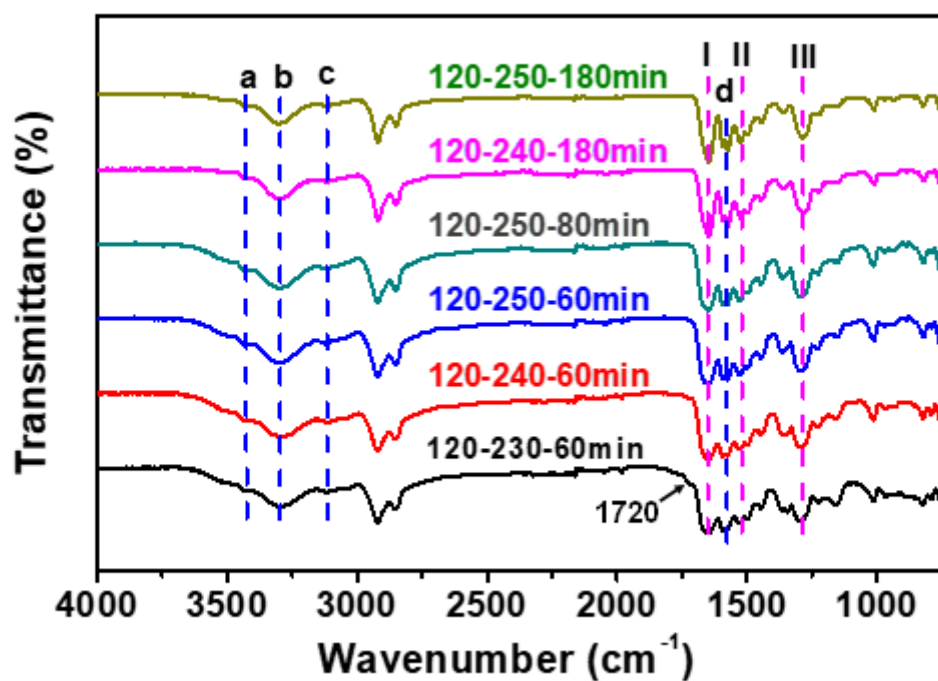


Figure 1

FT-IR spectra of PAFCHDM. (a) stretching vibration of free N-H; (b) stretching vibrations of hydrogen-bonded N-H groups; (c) C-H of furan stretching; (d) C=C stretching vibrations.

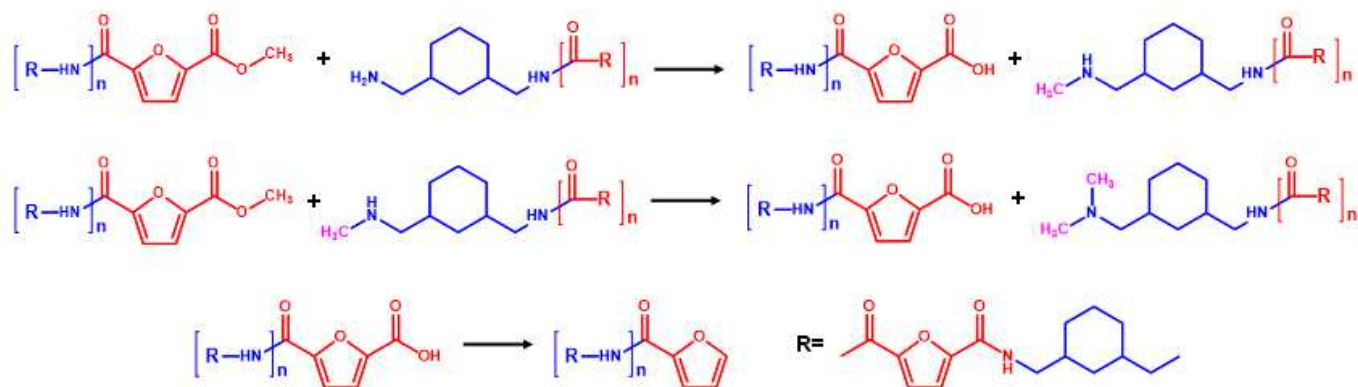


Figure 2

N-methylation and decarboxylation side reaction during the melt polymerization from DMFDCA and CHDM.

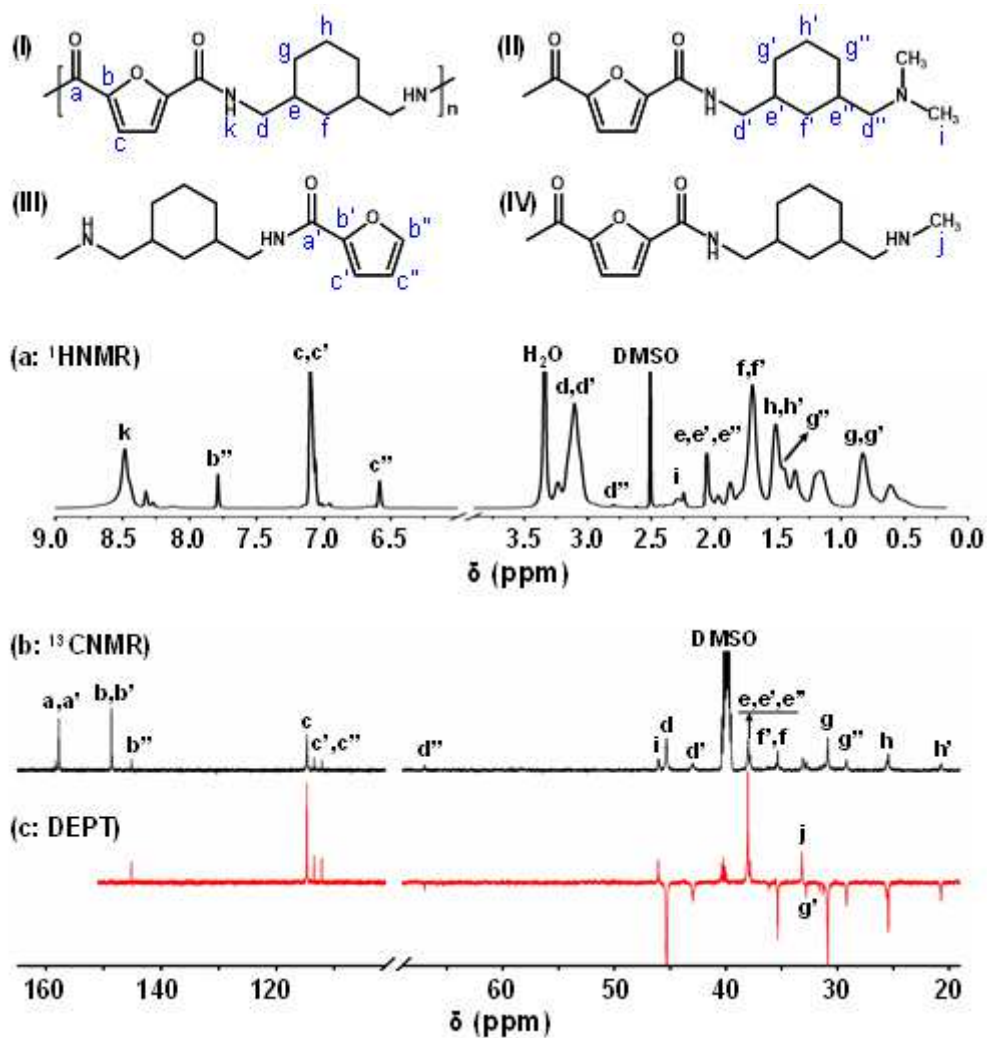


Figure 3

(a) ^1H NMR of the synthesized PAFCHDM, including three possible byproducts; (b) ^{13}C NMR of PAFCHDM, which was dissolved in DMSO- d_6 ; (c) DEPT spectrum of the PAFCHDM, DEPT spectroscopy is a type of carbon spectroscopy, is used to distinguish the primary carbon, secondary carbon, tertiary carbon and quaternary carbon.

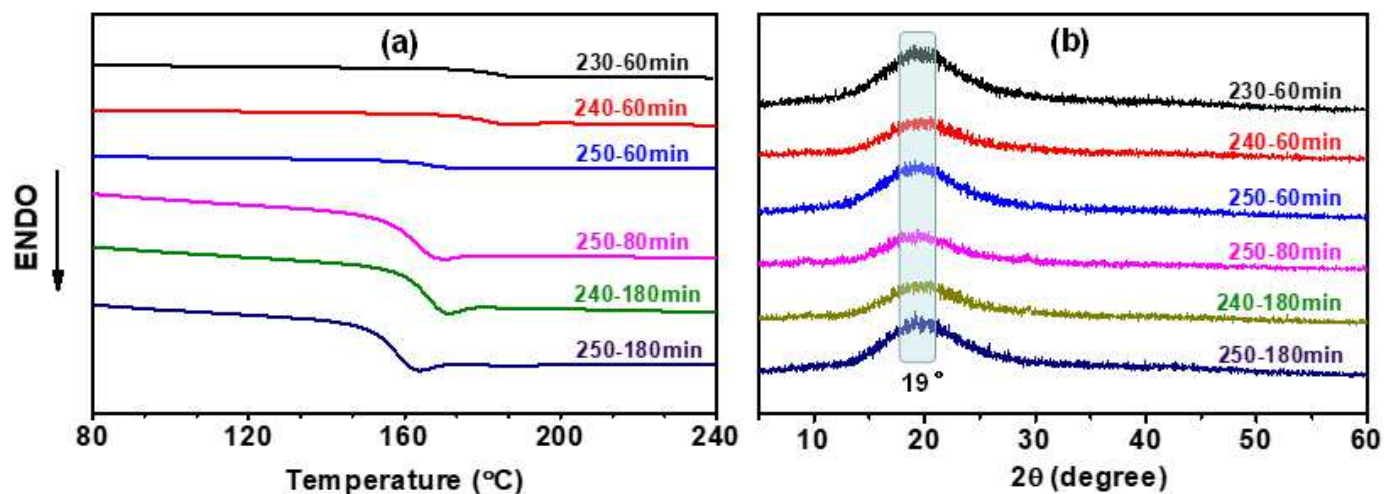


Figure 4

(a): Second heating curves of PAFCHDM from 80°C to 240°C under nitrogen; (b): XRD profiles of all the PAFCHDM samples.

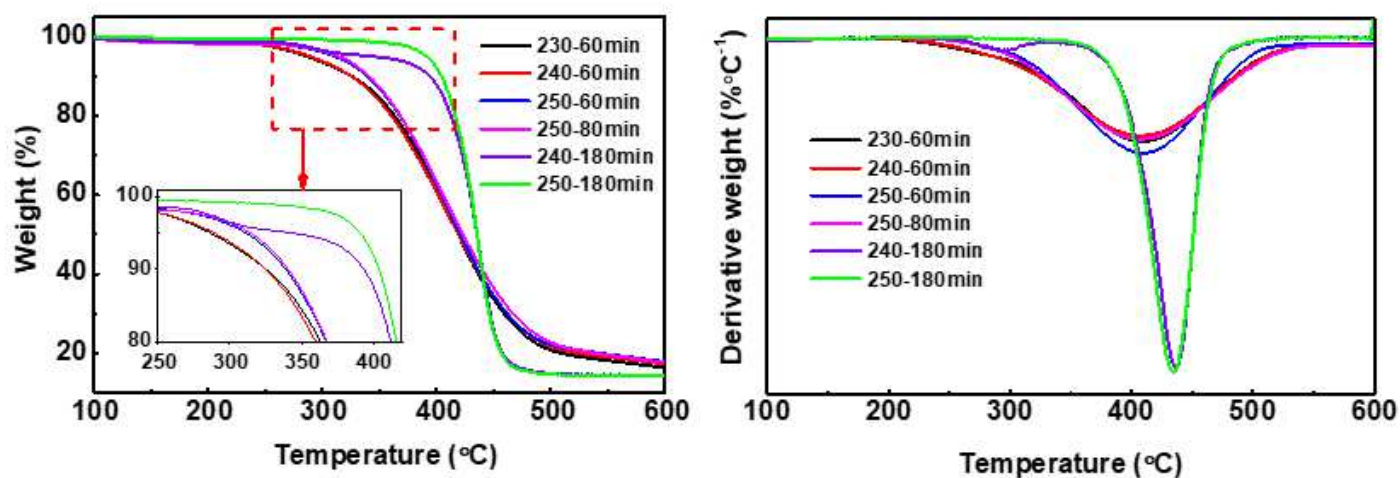


Figure 5

TGA (a) and DTG (b) curves of PAFCHDM, which is recorded from 100°C to 600°C under nitrogen.