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Sustainable Thermoplastics from Renewable Resources: Thermal behavior of Poly(1,4-cyclohexane dimethylene 2,5-furandicarboxylate)

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Abstract

Poly(1,4-cyclohexane dimethylene 2,5-furandicarboxylate) (PCHDMF) is a sustainable thermoplastic that can be prepared from renewable resources with potential uses as a replacement for its terephthalate (PCHDMT) and naphthalate (PCHDMN) analogues. A detailed study was undertaken to assess its thermal behavior and chemical/structural characteristics, in comparison to its counterparts. The melting temperature of PCHDMF was observed at $T_m=264.5^\circ\text{C}$, the glass transition was obtained at 77°C and the cold crystallization temperature was seen at 121°C . The melting of the polymers was studied under a variety of conditions and all samples displayed the characteristic melting-recrystallization-remelting behavior. Isothermal and dynamic crystallization tests revealed that PCHDMF crystallizes at faster rates than its analogues, while the equilibrium melting point of PCHDMF was established at 300°C . The enthalpy of fusion values for the polyesters were found $\Delta H_m=137\text{ J/g}$ for PCHDMF, $\Delta H_m=108\text{ J/g}$ for PCHDMT, $\Delta H_m=119\text{ J/g}$ for PCHDMN. Using the Lauritzen-Hoffman analysis of spherulite growth rates, larger K_g values were found for PCHDMF, due to its less flexible structure.

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1. Introduction

Polymers from renewable resources have gained an increasing interest last years [1-6]. Isosorbide, 2,4:3,5-di-O-methylene-D-mannitol, bicyclic diacetylated galactaric acid, 2,5-furandicarboxylic acid (FDCA), are among the most important monomers derived from biomass [7]. Especially 2,5-FDCA, shows good potential as a biobased replacement for terephthalic acid (TA) [8].

Terephthalic acid is a widely used monomer for the production of various polyesters of great industrial importance as it is used for a number of polymers, including poly(ethylene terephthalate) PET, poly(butylene terephthalate) (PBT) and poly(1,4-cyclohexane dimethylene terephthalate) (PCHDMT). On the other hand, 1,4-cyclohexanedimethanol is a diol that has been used in the production of polyesters with exceptional properties such as poly(1,4-cyclohexane dimethylene terephthalate) (PCHDMT) and poly(1,4-cyclohexane dimethylene naphthalate) (PCHDMN) [9-16]. The 1,4-cyclohexane dimethanol unit has two isomers, cis (equatorial-axial) and trans (axial-axial or equatorial-equatorial); the trans-form is more stable than the cis-form [17, 18].

2,5-FDCA or DMF-based polyesters have been attracting significant attention from both academia and industry due to their wide range of potential applications [19-21]. Poly(ethylene-2,5-furandicarboxylate) (PEF) has been known for more than 70 years and it was the first FDCA-based polyester to be studied [22-24]. PEF is possibly the most important member of the furan-family of polyesters, as it can be formulated in films, fibers and bottles [25-30].

Besides PEF, a series of furan-based polyesters, such as poly(propylene-2,5-furandicarboxylate) (PPF) and Poly(butylene-2,5-furandicarboxylate) (PBF) [31-34] have been synthesized and show very interesting properties as well, as alternatives to their terephthalate and naphthalate analogues.

Poly(1,4-cyclohexane dimethanol 2,5-furandicarboxylate) (PCHDMF) is a new and quite promising polyester. In contrast to PEF and the majority of furan-based polyesters, PCHDMF shows fast crystallization rates and only a few scientific papers have been published on PCHDMF and PCHDMF-related copolymers [35-41]. Potential

applications of PCHDMF include polymer fibers and packaging materials. Furthermore, PEF-based copolymers synthesized using 1,4CHDM have been reported to show favorable gas barrier properties [37].

Despite its advantageous properties and fast crystallization rates, the crystallization and melting behavior of PCHDMF has not been studied yet; in fact, almost the same holds for its counterparts PCHDMT and PCDMN. Therefore, in this work a complete investigation of the solid-state structure, the crystallization and the melting behavior of the three polyesters was carried out using wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The morphology of the three polymers was also studied in detail by using polarized light optical microscopy (PLOM). Important thermodynamic properties such as the enthalpy of fusion and equilibrium melting temperatures were also calculated.

2. Experimental

2.1. Materials

Dimethyl-2,6-naphthalate (DMN) was provided by Amoco Chemical Belgium (purity 98%) and dimethyl terephthalate (DMT) was obtained from Du Pont De Nemours Co. 2,5-furan dicarboxylic acid (purity 97 %), 1,4-cyclohexanedimethanol (CHDM, 70/30 trans/cis, purity 99%), and titanium (IV) isopropoxide (TIS) (purity 97%) catalyst were purchased from Sigma-Aldrich Chemical Co (Chemie GmbH, Germany). All other materials and solvents used were of analytical grade.

2.2. Synthesis of 2,5-dimethylfuran-dicarboxylate (DMF)

15.6 g of 2,5-furandicarboxylic acid, 200 mL of methanol anhydrite and 2 mL of concentrated sulfuric acid was transferred into a round flask (500 ml) and the mixture was refluxed for 5 hours. The excess of the methanol was distilled and the solution was filtered through a disposable Teflon membrane filter. During filtration dimethylester was precipitated as white powder and after cooling 100 mL of distilled water was added. The dispersion was partially neutralized by adding Na_2CO_3 5 % w/v during stirring while pH was measured continuously. The white powder was filtered and the solid was washed several times with distilled water and dried. The isolated white methylester was recrystallized with a mixture of 50/50 v/v methanol/water. After cooling 2,5-dimethylfuran-dicarboxylate (DMF) was precipitated in the form of white needles. The reaction yield was calculated at 83 %.

2.3. Polyester synthesis

The polyesters (Scheme 1) were prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [42].

For the preparation of poly(1,4-cyclohexane dimethylene terephthalate) (PCHDMT), the proper amounts of DMT and CHDM at a molar ratio of diester/CHDM = 1/2 with 400 ppm TIS were charged into the reaction tube of the polyesterification apparatus. The reaction mixture was heated at 230°C under argon atmosphere and was stirred at a constant speed (350 rpm). This first step (transesterification) is considered to be completed after the collection of almost all the theoretical amount of CH₃OH (about 2.5h), which was removed from the reaction mixture by distillation and collected in a graduate cylinder. Then the system was cooled down to room temperature and an equimolar amount of DMT was added. The added amount of DMT at this step was calculated considering that all initial DMT/CHDM amounts have been completely reacted and oligomers have been prepared. The reaction temperature was increased to 290°C and was set constant for 1h. In the second step of polycondensation vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min to remove the excess of diols and to avoid excessive foaming and furthermore to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was gradually increased during this period to 300°C while stirring speed was increased at 720 rpm. The polycondensation continued for about 1.5h at 300°C.

Poly(1,4-cyclohexane dimethanol 2,5-furandicarboxylate) (PCHDMF) was synthesized as described previously using the proper amounts of DMF and CHDM at a molar ratio of diester/CHDM = 1/2 and 400 ppm TIS. The reaction mixture was heated under argon atmosphere and stirred at a constant speed (350 rpm) at 240°C for 1h. Then, the temperature was gradually increased to 260°C and the mixture was kept at this temperature for 1.5h to finish the first step of transesterification. The second step took place under high-vacuum conditions, at 270°C for 2.5h. The intrinsic IV of the prepared polyester was measured at 0.46 dL/g.

The synthesis of PCHDMN was carried out according to the method described in our previous work [16] wherein 2,6-DMN and CHDM at a molar ratio of 2,6-DMN/CHDM=1/1 were charged in a glass batch reactor with 400 ppm TIS. In the first stage of transesterification, the reaction mixture was heated at 270°C for 0.5 h under nitrogen atmosphere. In the second step of polycondensation, the pressure was reduced

(5.0 Pa) and the reaction temperature was kept at 290°C for 1h. The prepared IV was 0.56 dL/g.

Scheme I. Chemical structures of the PCHDMF, PCHMDT, and PCHDMN polyester

2.4. Polyester characterization

2.4.1. Intrinsic viscosity measurement.

Intrinsic viscosity $[\eta]$ measurements were performed using an Ubbelohde viscometer at 25°C in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40, w/w). The samples were kept in the above mixture of solvent at 70°C for 20 min to reach complete dissolution. The solution was then cooled down to ambient temperature and filtered using a disposable membrane filter (Teflon) to remove any non-soluble materials. Three different measurements were carried out, and the average value was calculated.

The IV of the prepared PCHDMF polyester was equal to 0.46 dL/g. For PCHDMT and PCHDMN samples the measured IV values were 0.51 and 0.56 dL/g.

2.4.2. Wide angle X-Ray diffraction patterns (WAXD).

X-ray diffraction measurements of the samples were performed using a MiniFlex II XRD system from Rigaku Co, with $\text{CuK}\alpha$ radiation ($\lambda=0.154$ nm) in the angle 2θ range from 5 to 60 degrees.

2.4.3. Nuclear Magnetic Resonance (NMR)

^1H -NMR spectra of prepared polyesters were recorded using a Bruker spectrometer operating at a frequency of 500 MHz. Deuterated trifluoroacetic acid (d-TFA) was used as solvent to prepare solution of 5% w/v. The number of scans was 10, and the sweep width was 6 kHz.

2.4.4. Differential scanning calorimetry (DSC)

Thermal analysis studies were carried out using a Perkin Elmer Diamond DSC updated to DSC 8500 level, combined with a Intracooler IIP cooling system. Samples

of about 5 mg were used. The samples were first heated at 20°C/min to a temperature 40 °C above the melting peak temperature, to erase the previous thermal history. To record the glass transition, the samples were first melt quenched on a frozen metal plate and then were put in the DSC cell. In general heating scans of the samples were conducted at 20°C/min. To study the crystallization on cooling from the melt scans at different rates were performed.

Isothermal crystallization experiments of the polymers at various temperatures below the melting point were performed after self-nucleation (SN) of the polyester sample. The SN procedure leads to enhanced crystallization rates, so that it allows crystallizations to be performed even in case of very small supercoolings, that is at temperatures close to the melting temperature. As a result, crystallizations were tested in a wide temperature range. Self-nucleation measurements were performed in analogy to the procedure described by Fillon *et al.* [43]. The protocol used was very similar with that described by Müller *et al.* [44] and can be summarized as follows: a) melting of the sample at 40 °C above the observed melting point for 5 min to erase any previous thermal history; b) cooling at 10 °C/min to a reference temperature and crystallization, to create a “standard” thermal history; c) partial melting by heating at 20 °C/min up to a “self-nucleation temperature”, T_s which differed for the various polymers; d) thermal conditioning at T_s for 5 min. Depending on T_s , the crystalline polyester will be completely molten, only self-nucleated or self-nucleated and annealed. If T_s is sufficiently high, no self-nuclei or crystal fragments can remain. At intermediate T_s values, the sample is almost completely molten, but some small crystal fragments or crystal memory effects remain, which can act as self-nuclei during a subsequent cooling from T_s . Finally, if T_s is too low, the crystals will only be partially molten, and the remaining crystals will undergo annealing during the 5 min at T_s , while the molten crystals will be self-nucleated during the following cooling; e) cooling scan from T_s at 200 °C/min to the crystallization temperature (T_c), where the effects of the previous thermal treatment will be reflected on isothermal crystallization; f) heating scan at 20 °C/min to 40 °C above the melting point, where the effects of the thermal history will be apparent on the melting signal. Experiments were performed to check that the sample did not crystallize during the cooling to T_c and that a full crystallization exothermic peak was recorded at T_c . In heating scans after isothermal crystallization, the standard heating rate was 20 °C/min. In some specific cases, heating experiments at different rates after isothermal crystallization was also carried out to better

understand the melting behaviours of the polyesters. For the three polymers of this work the best choice for T_s was found to be $T_s = T_{\text{mend}} - 2$, where T_{mend} is the temperature at the end of the melting peak. For example, for PCHDMF $T_{\text{mend}} = 269\text{ }^{\circ}\text{C}$ and $T_s = 267\text{ }^{\circ}\text{C}$. Tests showed that at higher T_s values the polyester was completely molten. On the other hand, annealing was observed at temperatures lower than $T_s = T_{\text{mend}} - 2$.

To investigate the non-isothermal crystallization of the polyesters from the melt, the same melting procedure as described above for the isothermal crystallization was followed and then the samples were cooled from the melt under a wide range of cooling rates, from 0.1 to 20 $^{\circ}\text{C}/\text{min}$.

2.4.5. Polarizing light microscopy (PLM).

A polarizing light microscope (Nikon, Optiphot-2) equipped with a Linkam THMS 600 heating stage, a Linkam TP 91 control unit and also a Jenoptic ProgRes C10Plus camera were used for PLM observations.

3. Results and Discussion

3.1 Solid state structure

The chemical structures of the prepared polyesters, namely PCHDMF, PCHMDT and PCHDMN were confirmed by ^1H -NMR spectroscopy, displaying the characteristic resonances attributed to the protons of the resulting materials as shown in Figure 1a. The main differences observed in the ^1H -NMR spectra of these polymers arise from their aromatic units, viz.: a resonance associated with the furan ring protons (a) appeared as a singlet peak at 7.46 ppm for PCHDMF. A resonance at 8.27 ppm attributed to the terephthalic protons (a) as well as other resonances have been observed at 8.28 ppm and 8.83 ppm respectively, assigned to the naphthalene ring protons (a) and (b) of PCHDMN. The common CHDM moiety incorporated into the structure of the three polyesters has displayed exactly the same chemical shifts for its corresponding characteristic protons, viz.: two peaks at 4.51 and 4.64 ppm were respectively attributed to the trans- and cis-methylene protons in CHMD, labelled as (b) for PCHMDT and PCHDMF and (c) for PCHDMN. The resonances ranging from 1.33 to 2.23 ppm were associated with the CH_2 and CH protons of CHDM ring tagged (c) and (d) for PCHDMF and PCHMDT whereas labelled (e) and (d) for PCHDMN, wherein their chemical shifts are dependent on the equatorial (eq) or axial (ax)

substitution of the trans/cis isomers. The detailed indexation of (c) and (d) protons for PCHDMT and PCHDMF and (d) and (e) for PCHDMN is also shown in Figure 1a, which is in well accordance with the one found in the study of Hong *et al.* [38].

The WAXD pattern for PCHDMF presented in Figure 1b is typical of a semicrystalline polyester. The strong crystal reflections appear at 16.7° , 20.8° , 22.2° , while weak peaks appear at 9.8° , 30.7° , and 43.6° . Very weak peaks can be also seen at 15.0° , 26.9° and at 33.5° . In fact, it is quite difficult to obtain amorphous specimens from the particular polymer. For the case of PCHDMT, the samples show peaks from reflections at 15.1° , 16.7° , 19.1° , 23.5° and 25.6° , which correspond to Miller indexes of (011), (010), ($\bar{1}\bar{1}0$), (100) and ($\bar{1}\bar{1}1$) [45]. Finally, the diffractogram of PCHDMN, shows reflections at 14° , 15.7° , 17.5° , 18.4° , 20.7° , 23.4° , and 26.4° , corresponding to diffractions from the (011), (010), ($\bar{1}\bar{1}1$), ($\bar{1}\bar{1}2$), ($\bar{1}\bar{1}0$), (100) and ($\bar{1}\bar{1}\bar{1}$) planes [46].

Figure 1. a) ^1H NMR spectrum for PCHDMF, b) WAXD patterns for PCHDMF, PCHDMT and PCHDMN and c) deconvolution procedure to calculate the degree of crystallinity for PCHDMF.

By using the WAXD patterns and after the deconvolution of the crystalline part over the amorphous halo of the polymers (Figure 1c), the degree of crystallinity values were calculated for several samples for each polymer, after crystallization at different conditions. Firstly, the samples were melt-quenched. As the polymers crystallize fast, each of the quenched samples was heated at $20^\circ\text{C}/\text{min}$ up to a

predetermined temperature above the T_g to crystallize in controlled manner. The ultimate temperature changed from sample to sample, to obtain samples with different degrees of crystallinity.

The crystallinity values were calculated from the WAXD patterns along with the relative areas under the crystalline peaks, A_c , and the amorphous background, A_{am} , using the following equation:

$$X_c = (1 + A_{am}/A_c)^{-1} \quad (1)$$

according to Hay *et al.* [47].

The values of the heat of fusion measured using DSC were plotted as a function of the degree of crystallinity and finally the enthalpy of fusion values for the pure crystalline samples were determined after extrapolation to 100% degree of crystallinity. The obtained values were $\Delta H_m=137$ J/g or 36.17 kJ/mol for PCHDMF, $\Delta H_m=108$ J/g or 29.59 kJ/mol for PCHDMT and $\Delta H_m=119$ J/g or 38.56 kJ/mol for PCHDMN.

3.2 Thermal Characteristics

The DSC thermograms recorded at 20°C/min for the semicrystalline and melt-quenched samples of PCHDMF (Figure 2a) show a melting peak temperature of $T_m= 264.5^\circ\text{C}$ and a glass transition temperature of $T_g= 77^\circ\text{C}$. For the melt quenched sample, a sharp cold-crystallization peak appears at $T_{cc}= 121^\circ\text{C}$. The melting temperature and glass transition temperature of PCHDMF are observed at lower temperatures than those for poly(1,4-cyclohexane dimethylene 2,5-terephthalate) (PCHDMT) which shows a T_m at 293°C and a T_g at 80°C . The T_{cc} is 118°C for PCHDMT, somewhat lower than that for PCHDMF (Figure 2b). These results show that PCHDF crystallizes less easily than PCHDMT, considering the difference $\Delta T= T_{cc} - T_g$. Moreover, as it was expected, PCHDMN melts at the highest temperature of all three polymers ($T_m= 318^\circ\text{C}$), most probably because of π - π stacking/van der Waals interactions between naphthalene rings, crystallized at $T_{cc}= 165^\circ\text{C}$, while its glass transition was observed at $T_g= 118^\circ\text{C}$ (Figure 2c). The larger naphthalene rings of PCHDMN (compared to the furanoate and benzene ones) are stiffer as a result of their structure that does not allow a rotation of the rings and that is why PCHDMN displays the highest melting point and glass transition of all three polymers.

Figure 2. DSC thermograms for (a) PCHDMF, (b) PHDMT and (c) PCHDMN. The direction of endotherm is up.

3.3 Isothermal Crystallization

The isothermal crystallization from the melt was studied for various temperatures in the range from 200°C to 245°C for PCHDMF. The relative degree of crystallinity with increasing time can be obtained if the assumption that the evolution of crystallinity is linearly proportional to the evolution of heat during the crystallization [24]:

$$X(t) = \frac{\int_0^t (dH_c / dt) dt}{\int_0^\infty (dH_c / dt) dt} \quad (1)$$

where dH_c denotes the measured enthalpy of crystallization during an infinitesimal time interval dt . Moreover, the limits t and ∞ on the integrals describe the elapsed time during the course of crystallization and at the end of the crystallization process, respectively. The evolution of the relative degree of crystallinity versus time over a wide range of isothermal crystallization temperatures for PCHDMF can be seen in

Figure 3a, while for the PCHDMT and PCHDMN samples it can be seen in Supplementary Information – Figure S1. The crystallization half-time ($t_{1/2}$) is an indication of the rate of crystallization and it represents the time when the material displays the 50% of its relative degree of crystallinity. The crystallization half-times were obtained therefore from Figure 3a and they are presented in Figure 3b-c versus the crystallization temperature and degree of supercooling, respectively. The supercooling (ΔT) is the difference between the equilibrium melting temperature T_m^o and crystallization temperature T_c , ($\Delta T = T_m^o - T_c$). As it can be seen, the crystallization half-times increase almost exponentially with temperature, a fact that shows that the crystallization rates decrease also in an exponential manner. As a matter of fact, at temperatures below 210°C, crystallization proceeds at very fast rates and the polymer crystallizes almost instantaneously. Both PCHDMT and PCDMN display an identical behaviour at higher temperatures; for PCHDMT the sample crystallizes at faster rates for $T_c < 260^\circ\text{C}$, while for PCHDMN faster crystallization rates are observed at $T_c < 297.5^\circ\text{C}$. Similarly, to the results from cold crystallization, PCHDMN displays the faster crystallization rates of all three samples, even though a direct comparison is difficult to be performed through isothermal crystallization, as the crystallization temperatures are different.

Figure 3. (a) Evolution of the relative degree of crystallinity versus time at a number of isothermal crystallization temperatures for PCHDMF, (b) evolution of isothermal crystallization half-time with temperature for all samples under study, (c) evolution of the crystallization half time with increasing degree of supercooling.

The subsequent DSC heating scans after the isothermal crystallizations are shown in Figure 4. As it can be seen up to four melting peaks appear upon heating for PCHDMF crystallized at temperatures below 225 $^{\circ}\text{C}$ (Figure 4a). Three peaks are observed for samples crystallized in the range 225-237.5 $^{\circ}\text{C}$, while two peaks are left in the traces for samples crystallized at T_c s up to 245 $^{\circ}\text{C}$. A small, low temperature endothermic peak (I) appears a few degrees above the crystallization temperature, as can be seen in the inset

of Figure 4a for the samples crystallized at 205°C. This is the well-known annealing peak [48]. The second peak (II) is followed by a recrystallization exothermic peak for samples crystallized at low T_c s, however it increases in peak area and temperature with increasing T_c . Peak III appears well above the crystallization temperature and steadily increases in peak temperature with increasing T_c . On the other hand, the ultimate temperature peak IV appears at almost unchanged temperature and finally coincides with peak III.

To evaluate the melting behavior of PCHDMF, samples crystallized at identical conditions were heated at different rates. The DSC heating scans of samples isothermally crystallized at 210 °C are shown in Figure 4b. As it can be seen, peaks II and III increased in both area and temperature with increasing heating rate. In contrast peak IV showed no change in temperature. The peak height ratios II/IV and especially III/IV increased with increasing heating rate. It should be also noted that the recrystallization exothermic peak always appeared just after peak II. In contrast, in the case of the thermograms of Figure 4c where the heating scans for samples crystallized at 225 °C are presented, the recrystallization exothermic peak disappeared in the traces for fast heating scans at 20 or 40 °C/min. Furthermore, peak II increased in both temperature and area in expense of peaks III and IV. Peak IV seemed to disappear with increasing heating rate. It can be concluded that peak II corresponds to the melting of primary crystals, while peak IV is associated with melting of the recrystallized material. Peak III might be also associated with recrystallized material. However, the melting for crystals with different stabilities (peaks I, II and III) grown during the isothermal stage cannot be totally precluded. These findings are consistent with the partial melting and recrystallization hypothesis which can be the origin of the multiple melting behavior of PCHDMF.

The same melting scheme can be concluded for both PCHDMT and PCHDMN (Figure 5 a,b). For T_c ranging between 230 and 260 °C three peaks appear for PCHDMT, as a result of the melting, crystallization and re-melting phenomenon occurring due to the formation of small, imperfect crystals at lower temperatures. For T_c higher than 265 °C, only one melting peak can be seen. Finally, for PCHDMN, three peaks appear for $T_c < 295$ °C, while from 300 °C and above the formed crystals are stable enough, so only two peaks appear, with the one being the annealing peak.

Figure 4. (a) DSC thermograms on heating at 20°C/min for PCHDMF after isothermal crystallization from the melt at the indicated temperatures. DSC heating scans at different heating rates for samples crystallized at (b) 210 °C and (c) 225 °C.

Figure 5. DSC thermograms on heating at 20°C/min for (a) PCHDMT and (b) PCHDMN samples after isothermal crystallization from the melt at the indicated temperatures.

3.3.1 Evaluation of the equilibrium melting temperature

The equilibrium melting temperature (T_m^0) is an important thermodynamic parameter for polymeric materials, as it represents the temperature from which the driving force for crystallization is defined. The extrapolative method of Hoffman and Weeks [49], is one of the simplest and most-used methods in literature for the evaluation of T_m^0 . In this method, the measured melting points of the samples crystallized at different temperatures are plotted against the crystallization temperature and the extrapolation of the linear fit to the $T_c = T_m$ line, the T_m^0 can be observed at the point of intersection. The Hoffman-Weeks theory is described by the equation:

$$T_m = T_m^o \left(1 - \frac{1}{\beta}\right) + \frac{T_c}{\beta} \quad (2)$$

where T_m is the observed melting temperature of a crystal formed at a temperature T_c , while β is the thickening parameter equal to L_c/L_c^* . The thickening parameter β indicates the ratio of the thickness of the mature crystallites L_c to that of the initial ones L_c^* [49].

There is considerable controversy on the literature over the validity of the Hoffman-Weeks equation, mostly because it is based on three major assumptions: a) the lateral dimensions should be much higher than the thickness of the lamellae, b) the thickening process occurs at a specific T_c and c) the thickening coefficient depends highly on the isothermal crystallization temperature [50]. The results from the application of this theory to the current experimental data can be seen in Figure 6 for all samples under study. The equilibrium melting point of PCHDMF was found equal to $T_m^0 = 300\text{ }^{\circ}\text{C}$, while the one of PCHDMT was $T_m^0 = 321\text{ }^{\circ}\text{C}$ and the one of PCHDMN was $T_m^0 = 352\text{ }^{\circ}\text{C}$. The number of aromatic rings and planarity in the naphthalate analogue of PCHDMF attributes significantly to the higher equilibrium melting point than that of PCHDMF and PCHDMT. Using these values in combination with those for the enthalpy of fusion, the corresponding values for the entropy of fusion were calculated as $\Delta S_m = 63.12\text{ kJ/mol}\cdot\text{K}$ for PCHDMF, $\Delta S_m = 49.82\text{ kJ/mol}\cdot\text{K}$ for PCHDMT and $\Delta S_m = 65.50\text{ kJ/mol}\cdot\text{K}$ for PCHDMT.

Figure 6. Hoffman-Weeks extrapolation for the estimation of the equilibrium melting point of PCHDMF.

3.4 Non-isothermal crystallization

The non-isothermal crystallization of PCHDMF was studied under a wide range of cooling rates, from 0.1 to 20 $^{\circ}\text{C}/\text{min}$. It was found that the higher the cooling rate, the broader the crystallization peak (Figure S2 – Supplementary Information). The

variation of the crystallization peak with increasing cooling rate can be seen in Figure 7 for all three samples under study, while the evolution of the relative degree of crystallinity versus temperature for PCHDMN and PCHDMT can be seen in Figure S3 – Supplementary Information.

Figure 7. Dependence of the crystallization peak temperature on the cooling rate for PCHDMF, PCHDMT and PCHDMN.

After non-isothermal crystallization, PCHDMF was heated at 5°C/min, in order to evaluate the effect of the cooling rate on the formed crystals. From the results presented in Figure 8, it is obvious that slow cooling rates enabled the formation of a larger amount of crystals as it can be realized from the respective enthalpies, which are directly related to the crystallinity. The lower enthalpy values were expected with increasing cooling rates, since the material has less time available to develop crystals; therefore, its degree of crystallinity is considerably lower than that when slower rates are used. The melting peak T_{m1} can be ascribed to the melting of the most stable original crystals formed during the cooling stage, which display the higher crystalline perfection and are indeed formed after the application of slow cooling rates. Of course, less stable crystals melt at lower temperature and then recrystallize. It can be seen that for rates ranging from 0.1 to 1°C/min, the T_{m1} is well-defined, while from that point on, the intensity and the area under the peak drop significantly. On the other hand, T_{m2} indicates melting of recrystallized material after the early melting a crystalline form with a less ordered structure than T_{m1} . Peak 2 appears only as a shoulder at the melting peak of the

sample cooled down with 0.1°C/min, while from that point on, it starts to develop. The same applies for T_{m3} , which appears with T_{m2} when cooling the sample with 0.5 °C/min and consistently develops with higher cooling rates, indicating that it is formed after recrystallization of a crystalline structure with lower perfection.

Figure 8. DSC heating scans at 5 °C/min after cooling at the indicated rates for PCHDMF.

3.5 Polarized Light Optical Microscopy (PLOM)

Polarized light optical microscopy (PLOM) was employed in order to study the morphology and the spherulitic growth rates of PCHDMF, PCHDMT and PCHDMN at a number of isothermal crystallization temperatures (Figures 9-11). As it can be seen in Figure 9 for the case of PCHDMF, the T_c plays a major role on the morphology of spherulites. At lower temperatures (T_c = 210, 220 °C) the well-rounded spherulites do not show clear rings and they are displaying the characteristic Maltese cross. However, with increasing crystallization temperatures, the morphology of the spherulites changes, which is an indication of a change in the crystallization regime of the polymer. The spherulites grown at 230 and 235 °C exhibit a ring-banded morphology without a maltese cross. Finally, further increasing the crystallization temperature above 240 °C, leads to elliptical shaped (probably axialitic) morphologies with an obvious distance between bands, and progressively more flat edges. The different structural characteristics between the three polymers, as they were observed by WAXD, can be also confirmed from the PLOM study. In the case of PCHDMT, the nucleation density

is higher than PCHDMF under equivalent supercoolings $\Delta T = T_m - T_c$, while the spherulites of the samples crystallized at 225-240 °C present a distorted ring banded morphology. Further increase of the crystallization temperature (250-270 °C), leads to crystals with higher structural perfection and the formation of axialites. Finally, for PCHDMN, as it can be seen from the images in Figure 11, the nucleation density is very high. Flat edges and elliptical shaped morphologies were observed at temperatures higher than 300 °C.

Figure 9. PLOM images for PCHDMF recorded at various isothermal crystallization temperatures.

Figure 10. PLOM images for PCHDMT recorded at various isothermal crystallization temperatures.

Figure 11. PLOM images for PCHDMN recorded at various isothermal crystallization temperatures.

3.6 Application of secondary nucleation theory using the spherulitic growth rates

The spherulitic growth rates for PCHDMF, PCHDMT and PCHDMN were determined during the PLOM study. Figure 12a shows the dependence of spherulite radius with time for PCHDMF. The spherulitic growth rates G , were measured as slopes of the

plots of the growing spherulite radius versus crystallization time, for a number of crystallization temperatures, ranging from 200 to 255 °C (Figure 12b).

Figure 12. (a) Dependence of the spherulite growth rate on temperature for PCHDMF, (b) Dependence of the spherulite radius on time at various temperatures for all samples under study

The kinetic data from isothermal crystallization can be analyzed with the Lauritzen-Hoffman secondary nucleation theory by using the spherulitic growth rate G [51]. In the theory, G is a function of the isothermal crystallization temperature according to the equation:

$$G = G_0 \exp\left[-\frac{U^*}{R(T_c - T_\infty)}\right] \exp\left[\frac{K_g}{T_c(\Delta T)f}\right] \quad (3)$$

where G_0 is the pre-exponential factor, the first exponential term describes the impact of diffusion process to the growth rate, while the second exponential term is the contribution of the nucleation process. Moreover, the U^* parameter denotes the activation energy which characterizes molecular diffusion across the interfacial boundary between melt and crystals, and T_∞ is the temperature below which diffusion stops. Also, the K_g is a nucleation parameter, while ΔT denotes the degree of undercooling ($\Delta T = T_m^0 - T_c$) and f is a correction factor which is close to unity at high temperatures and is given as $f = 2T_c/(T_m^0 + T_c)$ [51]. The equilibrium melting point of PCHDMF was set equal to 300 °C, while the glass transition was set equal to 77 °C, while various sets of values for U^* and T_∞ were tested. The growth rate can be determined by a single set of the constant parameters U^* and K_g ; for this reason, we have applied two different values of the activation energy that have been used widely in the literature and subsequently calculated the nucleation parameter. In general, for U^* and T_∞ the values $U^* = 6285$ J/mol and $T_\infty = (T_g - 30)$ K and also $U^* = 17600$ J/mol and $T_\infty = (T_g - 51.6)$ K have been proposed [52]. The value of $U^* = 6285$ J/mol is usually treated as the “universal value”, while Williams-Landel and Ferry [52] have proposed the value of $U^* = 17600$ J/mol based on a best fit approach. In order to calculate the nucleation parameter K_g , the double logarithmic transformation of Equation 3 is taken:

$$\ln(G) + \frac{U^*}{R(T_c - T_\infty)} = \ln(G_0) - \frac{K_g}{T_c(\Delta T)f} \quad (4)$$

the plot of the left-hand side of Equation 4 versus $1/T_c(\Delta T)$ can be fit with a straight line and the slope and intercept of this line will provide the nucleation constant and the pre-exponential factor respectively. The critical break points in the graph, which can be identified by the change in the slope of the line, indicate regime transitions accompanied by morphological changes of the formed crystals. Using the values of the spherulitic growth rate versus temperature, the Lauritzen-Hoffman plot was constructed for PCHDMF (Figure 13). As it can be seen in the graph, a break point always appears, corresponding to regime I to regime II in the range 241 to 244°C. Moreover, the K_{gI}/K_{gII} ratios depend on the applied set of U^* and T_∞ . For $U^* = 17600$ J/mol and $T_\infty = (T_g - 30)$ K the K_{gI}/K_{gII} ratio is very close to the expected value of 2.

The Lauritzen-Hoffman theory was also applied for PCHDMT and PCHDMN by using the spherulitic growth rates for both materials. The results are presented in Figures 14-15. As it can be seen, the two polymers do not present a regime transition. Regime I holds for temperatures very close to the melting temperature, while the regime which corresponds to the broader crystallization temperature range is regime II. Moreover, regime III corresponds to very large supercoolings, thus it was assumed that the regime II holds at the temperature range under study. The results from the application of the secondary nucleation theory for all samples can be seen in Table 1. As expected, in accordance with the theory suggested by Hoffman *et al.* [53], increasing the value of U^* leads to the evaluation of a larger value of K_g . The nucleation parameter K_{gII} is known to decrease with increase in chain flexibility, therefore it can be realised that the PCHDMT chains are more flexible than the ones of PCHDMN and PCHDMF, with the latter being the less flexible amongst the three.

Figure 13. Lauritzen-Hoffman plots for PCHDMF obtained from PLM measurements and displaying the characteristic regime transition, using various sets of U^* and T_∞ .

Figure 14. Lauritzen-Hoffman plots for PCHDMT obtained from PLM measurements and displaying the characteristic regime transition, using various sets of U^* and T_∞ .

Figure 15. Lauritzen-Hoffman plots for PCHDMN obtained from PLM measurements and displaying the characteristic regime transition, using various sets of U^* and T_∞ .

Table 1. The values of the nucleation parameter and the regime transition temperature (for PCHDMF) obtained after the application of the secondary nucleation theory.

Polyester	U^* (J/mol)	T_m^o (°C)	T_g (°C)	T_∞ (°C)	K_{gI} ($K^2 \times 10^5$)	K_{gII} ($K^2 \times 10^5$)	K_{gI}/K_{gII}	Regime Transition Temperature (°C)
PCHDMF	6285	300	77	$T_g - 30$	2.25	3.93	2.05	243
PCHDMF	6285	300	77	$T_g - 51.6$	2.2	3.74	1.7	244
PCHDMF	17600	300	77	$T_g - 30$	2.72	5.57	2.05	242
PCHDMF	17600	300	77	$T_g - 51.6$	2.59	5.03	1.94	243
PCHDMT	6285	321	80	$T_g - 30$	-	3.23	-	-
PCHDMT	6285	321	80	$T_g - 51.6$	-	3.16	-	-
PCHDMT	17600	321	80	$T_g - 30$	-	4.0	-	-
PCHDMT	17600	321	80	$T_g - 51.6$	-	3.77	-	-
PCHDMN	6285	352	118	$T_g - 30$	-	3.57	-	-
PCHDMN	6285	352	118	$T_g - 51.6$	-	3.49	-	-
PCHDMN	17600	352	118	$T_g - 30$	-	4.29	-	-
PCHDMN	17600	352	118	$T_g - 51.6$	-	4.08	-	-

4. Conclusions

Poly(1,4-cyclohexane-dimethylene 2,5-furanoate) was successfully synthesized using the melt polycondensation method and its thermal and structural characteristics were evaluated in detail. The structure of PCHDMF is typical of a semi-crystalline material,

while its melting point was found to be $T_m = 262\text{ }^{\circ}\text{C}$ and its glass temperature was $T_g = 77\text{ }^{\circ}\text{C}$. The heat of fusion of PCHDMF was estimated to be in the order of $\Delta H_m = 137\text{ J/g}$, while crystallization under isothermal and dynamic conditions revealed that PCHDMF crystallized at faster rates than its terephthalate and naphthalate counterparts. The melting behavior was studied under a wide range of heating/cooling rates and crystallization temperatures and the typical melting-recrystallization-remelting scheme was observed for all three polymers under study. The Hoffman-Weeks method was applied in order to calculate the equilibrium melting point of the three polymers and it was found that $T_m^0 = 300^{\circ}\text{C}$, for PCHDMF, while the one of PCHDMT was $T_m^0 = 321^{\circ}\text{C}$ and the one of PCHDMN was $T_m^0 = 352^{\circ}\text{C}$. Polarized light optical microscopy enabled us to observe the differences between the morphology of the spherulites at different isothermal crystallization temperatures and in this way, obtain the temperature at which the crystallization regime changes. This was also confirmed after the application of the Lauritzen-Hoffman secondary nucleation theory.

Data Availability: The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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Thermoplastics from Renewable Resources:
Crystallization and melting of
Poly(1,4-cyclohexane dimethylene 2,5-furandicarboxylate)

Figure S1. Evolution of the relative degree of crystallinity versus time at a number of isothermal crystallization temperatures for (a) PCHDMT and (b) PCHDMN

Figure S2. Non-isothermal crystallization curves of PCHDMF under a wide variety of cooling rates. The inset is a zoomed-in area of the crystallization peaks under very slow cooling rates.

Figure S3. Evolution of the relative degree of crystallinity versus time at a number of cooling rates crystallization temperatures for (a) PCHDMT and (b) PCHDMN

Figure S4. Spherulite radius versus temperature for PCHDMT at different annealing temperatures