Polymer 55 (2014) 2432–2439

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Aromatic thermotropic polyesters based on 2,5-furandicarboxylic acid and vanillic acid

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ARTICLE INFO

Article history:
Received 11 February 2014
Received in revised form
11 March 2014
Accepted 20 March 2014
Available online 27 March 2014

Keywords:
Thermotropic polyester
Renewable resources
2,5-Furandicarboxylic acid

ABSTRACT

This paper addresses a route to synthesize bio-based polymers with an aromatic backbone having a liquid crystalline (LC) phase in the molten state. The LC phase is employed to achieve uniaxial orientation during processing required in e.g. fiber spinning. For this purpose 2,5-furandicarboxylic acid (2,5-FDCA) and O-acetylvanillic acid (AVA), obtained from natural resources, are used as monomers. Similar to the 2,6-hydroxynapthoic acid used to perturb the crystalline packing of poly(oxybenzoate) in the Vectran® series, these bio-based monomers are used to lower the crystal to liquid crystal transition temperature. Considering that the poly(oxybenzoate) can also be obtained from natural resources, the adopted route provides the unique possibility to synthesize bio-based polymers that can be used for high performance applications. To obtain the desired polymers, a synthetic route is developed to overcome the thermal instability of the 2,5-FDCA monomer. Experimental techniques, such as optical microscopy, FTIR spectroscopy, DSC, and TGA are employed to follow the polymerization, phase transitions and evaluate thermal stability of the synthesized polymers.

1. Introduction

Over the last decades, extensive research has been performed to develop fully aromatic liquid crystalline (LC) polymers. The excellent mechanical and thermal properties, chemical resistance, and ease of processing in the (nematic) LC phase have led to the development of numerous polymers showing LC behavior. Commercial examples of such high performance LC polymers are the Twaron® or Kevlar® polyamides and the Vectra® polyesters. However, a wide variety of other main-chain LC polymers have been developed and reviewed extensively by Han and Bhowmik [1], Ballauff [2], Windle [3], and others [4–8].

Although some examples of lyotropic polyesters are reported by Lin [9] and Polk [10], most research focuses on the thermotropic polyesters since these materials can be processed from their melt and do not require expensive solvents and solvent recovery systems. However, thermotropic homopolyesters often have a high crystal to liquid crystal transition temperature, making processing from the LC melt challenging and often unattractive from a practical perspective. [11] Very often, structural modifications are required to lower the melting temperatures of LC polymers, in order to decrease processing costs and prevent thermal degradation. The most common examples of such modifications are the copolymerization of other mesogenic monomers, the usage of bulky substituents, the incorporation of flexible spacers, or the copolymerization of non-linear monomers [12–15]. For example, Cottis et al. [16] showed in 1972 the perturbing effect of the copolymerization of the linear monomers hydroquinone (HQ) and terephthalic acid (TA) with hydroxybenzoic acid (HBA) and reported polymers with lower crystal to liquid crystal transition temperatures. The copolymerization of the mesogenic crankshaft monomer 2,6-hydroxynaphthoic acid with HBA was reported in 1978 by Calundann [17], yielding a random copolymer with a melting temperature below 330 °C. An example of the usage of the kinked monomer isophthalic acid was reported by Nagano and Nomura [18] in 1999 and is commercially available as Sumikasuper LCP. Examples of the applications of other non-linear monomers such as m-HBA or different diols are found in the publications of Ballauff [19], Griffin [20], and Kricheldorf [21]. The last approach to lower melting temperatures of thermotropic homopolyesters is to include

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http://dx.doi.org/10.1016/j.polymer.2014.03.033
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flexible spacers into the polymer backbone. One example of such an approach was reported by Jackson [22] in 1976, where he showed the liquid crystalline nature of polymers based on PET and HBA.

Most of the early reports on thermotropic polyesters involve the usage of substituted benzene, biphenyl or naphthalene derivatives to perturb the poly(oxybenzoate) (POBA) backbone, leading to the formation of a non-periodic layer adjacent to the crystalline lattice. The very nature of the non-periodic layer has been a subject of independent studies by Blackwell [23] and Windle [24] in the past. In this publication, inspired by the earlier studies to perturb the crystal lattice, the possibility to introduce aromatic bio-based moieties into the POBA backbone is investigated. The perturbation is likely to decrease the melting temperature and promote processing from the LC melt. The bio-based monomers used in this study are 2,5-furandicarboxylic acid (2,5-FDCA) [25] and O-acetylvanillic acid (4-acetoxy-3-methoxybenzoic acid, AVA). The copolymerization of small amounts of AVA in thermotropic polyesters has been widely investigated and is known to increase the uniaxial deformation, mechanical properties, solubility and glass transition temperature of PET- and HBA-based LC polyesters [26–28]. The usage of 2,5-FDCA in thermotropic polyesters has been reported in patent applications by Vriesema [29] and Fujioka [30]. Vriesema showed that the replacement of small amounts of TA by 2,5-FDCA causes a decrease in the melting temperature while retaining the thermotropic behavior of the polymer. Fujioka copolymerized 2,5-FDCA and a phosphorous containing diol with HBA to synthesize heat resistant LC polyesters. Both of these inventions use 2,5-FDCA as a co-monomer in POBA-based LC polyesters. However, the crystal to LC transition temperature of the designed thermotropic polyesters exists only above 300 °C.

Although reports on the usage of 2,5-FDCA as a monomer in thermotropic polyesters are limited, the usage of other five membered heterocyclic rings such as pyridazine [31], thiadiazole [32], oxadiazole [33–35], and imidazole [36] are widely applied in liquid crystals and liquid crystalline polymers. Furthermore, the usage of 2,5-thiophenedicarboxylic acid (2,5-TDCA), a heterocyclic monomer similar to 2,5-FDCA, is reported by Cai, Preston and Samulski [37]. These authors showed that the usage of 2,5-TDCA as replacement of TA resulted in a decrease in melting temperature without losing the liquid crystalline nature of the polymer. Interestingly, unlike furan [38], both the thiophene and oxadiazole moiety are of a mesogenic nature, allowing for the synthesis of non-linear structures exhibiting thermotropic melt-behavior [26]. Since the 2,5-furandicarboxylate moiety itself is not a mesogen, we use 4,4′-biphenol and hydroxybenzoic acid to ensure the thermotropic melt-behavior of the polymers synthesized in this study.

It is acknowledged that 2,5-FDCA tends to undergo side reactions leading to increasingly discolored products with increasing reaction temperatures between 200 and 275 °C [39]. As early as 1946, Drewitt and Lincoln [40] noticed that 2,5-FDCA is prone to decarboxylate and evolve CO_2 at the applied reaction temperatures, which ranged between 220 and 280 °C. Thus the decarboxylation and degradation of 2,5-FDCA limits the reaction and processing temperatures. For this reason, we aim to investigate the viability of the heterocyclic 2,5-FDCA as a monomer in fully aromatic thermotropic liquid crystalline polyesters (TLCPs). Considering the polymerization temperature as the limiting factor, in this publication, a series of polymers containing 2,5-FDCA exhibiting LC behavior in the temperature window of 200 °C–300 °C are synthesized and characterized [41].

The thin-film polymerization (TFP) method reported by Cheng et al. [42] is used to screen the incorporation of variable amounts of 2,5-FDCA into the POBA backbone and its influence on the evolution of the LC phase. A similar approach was performed by Xu and coworkers [43] to study the incorporation of 2,5-TDCA. However, in this study, the thin-film polymerization is used to study different monomer compositions to find the composition and reaction parameters suitable for the synthesis of a 2,5-FDCA based thermotropic polyester, without degradation of the monomers. To suppress the melting and polymerization temperatures, the copolymerization of bio-based vanillic acid with 2,5-FDCA is performed. The composition and the polymerization of the monomers are monitored as a function of time using high temperature ATR–FTIR. Analysis of the polymers with interesting compositions is performed using TGA and DSC.

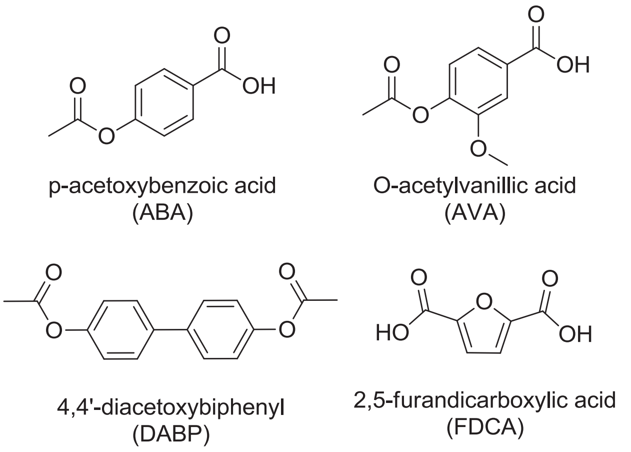

Fig. 1. Structural formulas of the monomers used in this study.

2. Experimental section

2.1. Materials

4-hydroxybenzoic acid and 4-hydroxy-3-methoxybenzoic acid were obtained from Sigma. The diol 4,4′-biphenol was purchased from TCI Europe. 2,5-Furandicarboxylic acid (99.5% purity, GC–MS) was ordered from Atomole (China). All monomers containing hydroxyl groups were acetylated and recrystallized at least once before polymerization. All other chemicals were used as received unless mentioned otherwise. The monomers used in this study are shown in Fig. 1.

2.2. General acetylation procedure

Ten grams of a monomer containing one or two hydroxyl groups were placed in a 100 mL round-bottom flask on a magnetic stirring plate. Acetic anhydride was added in a slight stoichiometric excess with respect to the hydroxyl groups together with a catalytic amount of H_2SO_4. The mixture was heated to 80 °C and stirred for 4 h. After cooling to 0 °C for 1 h 200 mL water was added to the mixture and the solution was filtered. The obtained crystals were washed with water and dried *in vacuo* at 40 °C overnight. All acetylated monomers were recrystallized at least once before usage in polymerization.

2.2.1. Preparation of 4-acetoxybenzoic acid (ABA)

4-acetoxybenzoic acid was prepared from 4-hydroxybenzoic acid (10 g, 72.4 mmol) and acetic anhydride (10 mL, 106 mmol) as described in the acetylation procedure. The resulting white powder was recrystallized twice from methanol to yield 8.44 g of product (64.7%). ^{1}H NMR (MeOD-d_4, δ, ppm): 8.06 (d, ArH, 2H), 7.21 (d, ArH, 2H), 4.91 (s, CO–OH, 1H), 2.30 (s, O–CO–CH_3, 3H). ^{13}C NMR (MeOD-d_4, δ, ppm): 170.57 (CH_3–**C**O), 169.00 (**C**OOH), 155.97 (Ar**C**–OAc), 132.27 (Ar**C**–COOH), 129.49 (Ar**C**), 122.90 (Ar**C**), 20.95 (CO–**C**H_3).

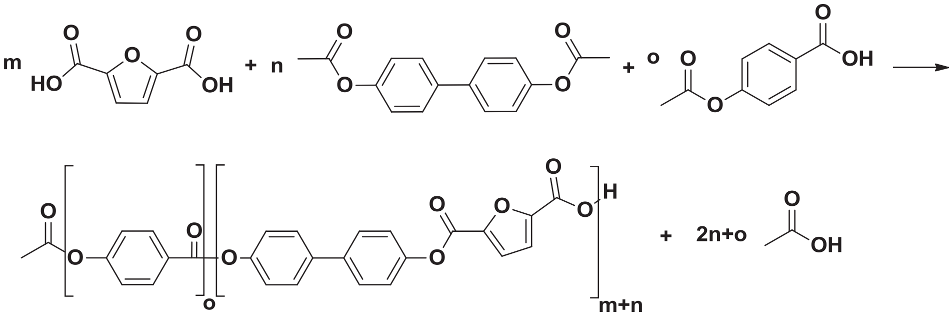

Fig. 2. Reaction scheme of the acidolysis polycondensation occurring in the 2,5-FDCA/DABP/ABA TFP systems. *N.b.* The resulting polymer can be of a random or blocky nature.

2.2.2. Preparation of 4-acetoxy-3-methoxybenzoic acid (AVA)

4-acetoxy-3-methoxybenzoic acid was prepared from 4-hydroxy-3-methoxybenzoic acid (10 g, 60.9 mmol) and 10 mL of acetic anhydride (106 mmol) as described in the acetylation procedure. The resulting slightly yellow powder was recrystallized twice from toluene to yield 9.34 g of product (72.9%). ^{1}H NMR (MeOD-$d_{4,}$ δ, ppm): 7.69 (d, ArH, 1H), 7.64 (dd, ArH, 1H), 7.12 (d, ArH, 1H), 3.86 (s, O–CH_3, 3H), 2.28 (s, CO–CH_3, 3H). ^{13}C NMR (MeOD-d_4, δ, ppm): 170.20 (CH_3–**C**=O), 169.02 (**C**OOH), 152.62 (Ar**C**–OCH_3), 145.11 (Ar**C**–OAc), 130.75 (Ar**C**–COOH), 123.88 (Ar**C**), 123.74 (Ar**C**), 114.51 (Ar**C**), 56.51 (O–**C**H_3), 20.46 (CO**C**H_3).

2.2.3. Preparation of 4,4′-diacetoxybiphenyl (DABP)

4,4′-dihydroxydiphenyl (10 g, 54 mmol) was acetylated as described in the general procedure to yield 11,2 g (77%) 4,4′-diacetoxybiphenyl after recrystallization from toluene. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.55 (d, ArH, 4H), 7.16 (d, ArH, 4H), 2.33 (s, C=O–CH_3, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 169.4 (CH_3–C=O), 150.1 (ArC–OAc), 138.1 (ArC–ArC), 128.1 (ArC), 121.9 (ArC), 21.1 (CO–CH_3).

2.3. Methods

Thin-film polymerizations (TFP)s monitored by polarization optical microscopy (POM) were conducted on a Zeiss Axioplan 2 Imaging optical microscope under crossed polarizers with or without a λ wave plate and CD achorplan objectives (20× or 32× Zoom). A THMS 600 heating stage connected to a Linkam TMS 94 control unit was mounted on the optical microscope. The monomers were dried overnight *in vacuo* at 40 °C, mixed and grinded twice before usage. Samples were prepared by placing 2–5 mg of a monomer mixture in between two glass slides with a ring spacer, where the sample was placed on the top glass slide. Samples were heated from room temperature with 100 °C/min to the desired reaction temperature and all reactions were conducted under a N_2 flow. The reaction time (t_r) is set to 0 when the desired reaction temperature was reached. Calibration of the temperature was performed using the melting temperatures of well-known compounds. Temperature calibration showed a 20 °C ± 3 °C difference from the input temperature and all temperatures mentioned in this publication are corrected values. The reactions were followed online and images were acquired every second.

ATR–FTIR measurements were performed on a Bio-rad FTS6000 FTIR Spectrometer with an ATR-plate connected to a high temperature golden gate with a maximum temperature of 300 °C. Samples were measured by the placement of 2–5 mg sample onto the hot plate at a fixed reaction temperature and spectra were collected online with intervals of 2 s using a liquid nitrogen-cooled WB MCT detector with a resolution of 4 cm^{-1}. A cover was placed on the top of the ATR-plate and was connected to N_2 flow to prevent evaporation and degradation of the monomers.

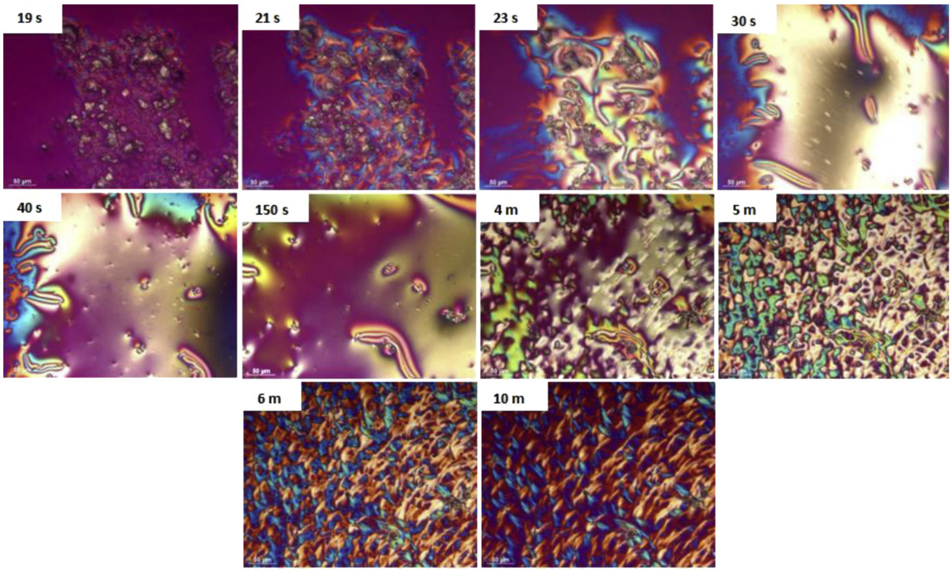

Fig. 3. Optical micrographs (in between cross-polars and red wave plate) showing the transitions from isotropic to the liquid crystalline and to the crystalline phase during the TFP of the 2,5-FDCA/DABP/ABA 15/15/70 reaction system at 300 °C. The mentioned time on the micrographs refers to the reaction time (t_r).

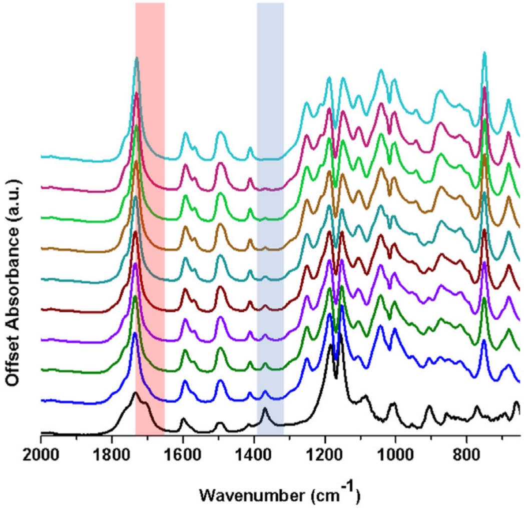

Fig. 4. Overview of the ATR–FTIR spectra collected with the increasing polymerization time between 2000 and 650 cm^{-1} obtained during a TFP of the 2,5-FDCA/DABP/ABA 15/15/70 system at 300 °C.

Thermal decomposition studies were performed on a TA instruments TGA Q500 machine under N_2 rich atmosphere. Samples were heated at 20 °C/min from 20 °C to 800 °C. Temperature calibration was performed using the Curie points of high-purity aluminum, nickel and perkalloy standards.

The thermal behavior of the samples was studied using a TA instruments Q1000 DSC. The apparatus was calibrated using indium and aluminum oxide. The normal heating and cooling-rates of the samples were 10 °C/min and measurements were performed under a N_2 rich atmosphere.

3. Results and discussion

3.1. Phase behavior of 2,5-FDCA/DABP/ABA system

The thin-film polymerization (TFP) method, described by Cheng [42], was used to follow the influence of the copolymerization of 2,5-furandicarboxylic acid (2,5-FDCA) and 4,4-diacetoxybiphenyl (DABP) on the LC behavior during a polymerization of *p*-acetoxybenzoic acid (ABA). Different compositions of 2,5-FDCA, DAPB and ABA were screened along a broad temperature range between 220 °C and 380 °C, and the morphological changes were followed via polarization optical microscopy. Fig. 2 shows the reaction scheme of the polycondensation reaction occurring in the thin-film polymerization of 2,5-FDCA/DABP/ABA systems. During this reaction, polymerization proceeds through an acidolysis reaction, forming acetic acid as the condensate. Fig. 3 shows an example of the development of the morphology during the ongoing polymerization of the 2,5-FDCA/DABP/ABA 15/15/70 system at a reaction temperature of 300 °C. All micrographs were taken from the same area of the sample over time, under isothermal condition. The micrographs show the typical morphological changes occurring during the synthesis of high melting, thermotropic polyesters. During this process, transformation of the isotropic phase to the LC phase (t_r ∼ 20 s) is observed, followed by the coalescence and homogenization of the LC phase (t_r ∼ 20–60 s) and crystallization ($t_r > 4$ min). Melting of the crystals thus obtained in the 2,5-FDCA/DABP/ABA 15/15/70 system is observed at 380 °C upon heating at 10 °C/min. Unfortunately, because of the rapid degradation of the monomers, TFP to follow the development and morphology of the LC melt of the 2,5-FDCA/DABP/ABA 15/15/70 at 380 °C could not be performed.

Fig. 3 shows that the formation of the LC droplets occurs (t_r = 19–23 s) prior to the full dissolution of the 2,5-FDCA crystals, indicating that the 2,5-FDCA is poorly soluble in the monomer/oligomers mixture. It is expected that the poor solubility of the 2,5-FDCA allows the reaction to progress simultaneously with the dissolution of the 2,5-FDCA crystals, i.e. polymerization initiates on the surface of the 2,5-FDCA crystals. Hence, during polymerization, the crystals react and dissolve from the outside in. The rate of the reaction will thus be limited by the reaction temperature, by the availability of reactive groups, and by the surface to volume ratio of the 2,5-FDCA crystals.

Similar behavior was observed by Economy during copolymerizations of ABA with terephthalic acid (TA), and 4,4′-biphenol [11]. This author showed that the poor solubility of TA resulted in the formation of oxybenzoate/4,4′-biphenol-rich domains. Rapid crystallization of the system prohibited the transesterification in the LC melt and led to a high degree of phase segregation of the monomers in the form of blocks in the final polymer. This slow dissolution behavior of TA was confirmed by Cheng et al. [44] during the TFP of ABA/BP/TA systems.

It is expected that the polymers obtained during the TFP of 2,5-FDCA/DABP/ABA systems exhibit a high degree of block formation, similar to the systems studied by Economy. The LC droplets formed

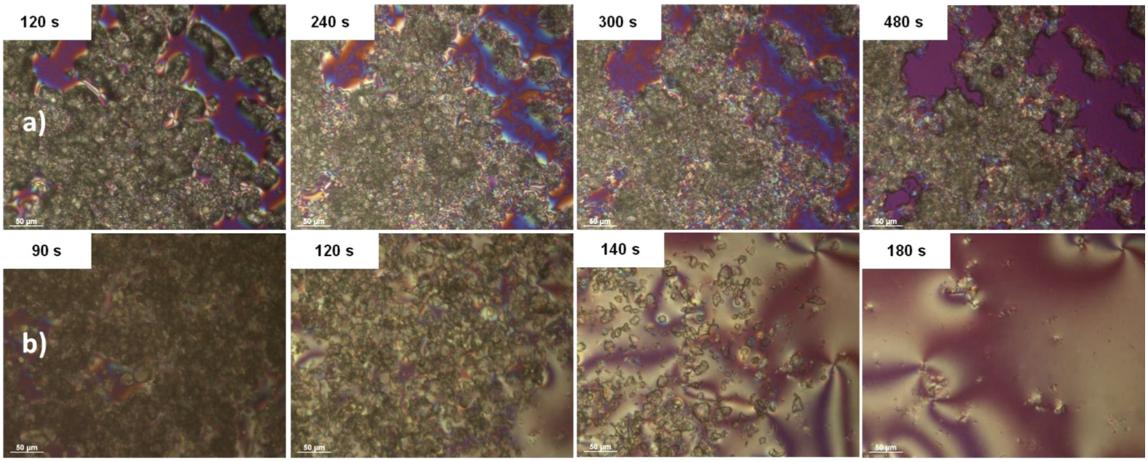

Fig. 5. Optical micrographs showing the morphological changes of the LC phase formation during the TFP of the 2,5-FDCA/DABP/ABA 35/35/30 reaction system under isothermal condition at a) 280 °C and b) 300 °C.

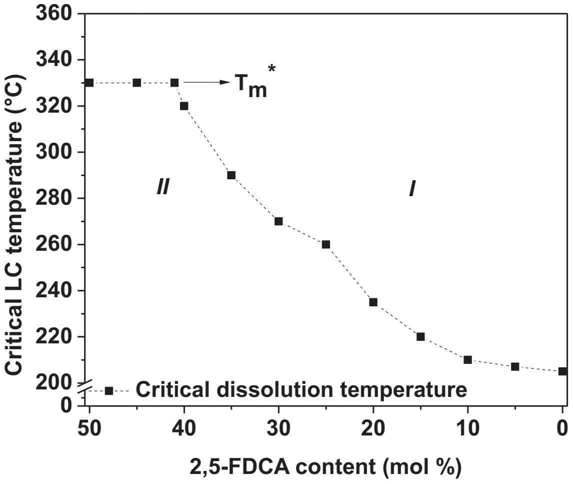

Fig. 6. The decrease of the critical dissolution/reaction temperatures as a function of the 2,5-FDCA content in the 2,5-FDCA/DABP/ABA systems. The ratio of 2,5-FDCA/DABP is kept equimolar. The T_m* denotes the temperature where all visible 2,5-FDCA crystals are molten/dissolved at the start of the reaction, independent of the amount of 2,5-FDCA present in the system (>330 °C).

in the initial phase of polymerization have an oxybenzoate/4,4′-biphenol rich composition, due to the unavailability of 2,5-FDCA in the liquid phase. The phase transformation from LC to crystal phase occurs once the 2,5-FDCA monomers have fully reacted. The blocky nature of the formed polymer is maintained since trans-esterification from the melt is prevented by the rapid crystallization (>4 m, Fig. 3).

To follow the incorporation of the 2,5-FDCA monomer into the polymer backbone, a TFP was followed with time using ATR–FTIR at 300 °C (Fig. 4). The FTIR results show a rapid decrease of the signal for the CH_3 vibration band of the acetoxy end-group at 1376 cm^{-1} (C=O–CH_3), the carbonyl stretch band of the acetoxy end-group at 1770 cm^{-1}, and carbonyl stretch band of the free acid group at 1703 cm^{-1}. This indicates that the concentration of the reactive end-groups decreases with polymerization. Simultaneously, the increase of the signal of the aromatic ester carbonyl stretch band at 1735 cm^{-1} indicates that the aromatic ester groups are formed, thus polymerization occurs. The incorporation of 2,5-FDCA in the final polymer can be detected by the presence of bands at 943 and 1567 cm^{-1} corresponding to the vibrations of the furan ring [45].

The presence of the insoluble 2,5-FDCA limits the polymerization rate at low reaction temperatures or in reactions with a very high 2,5-FDCA content. The time required for the 2,5-FDCA to fully dissolve and participate in the reaction increases with the increasing 2,5-FDCA concentrations and thus extends the reaction time. However, with the extended reaction times, the oxybenzoate/4,4′-biphenol rich blocks will have more time to build-up molecular weight and will be able crystallize during polymerization. Fig. 5a shows an example of the polymerization of the 2,5-FDCA/DABP/ABA 35/35/10 system at 280 °C where, due to the presence of undissolved 2,5-FDCA crystals, polymerization cannot be completed. Fig. 5a shows that at 280 °C, the formation of an LC phase is visible after 120 s, but does not develop over the whole view area. Instead, the LC domains crystallize and the undissolved 2,5-FDCA crystals remain present (t_r = 480 s). When the same reaction is conducted at 300 °C, a full dissolution and simultaneous reaction of the 2,5-FDCA monomers is achieved over time and the development of a homogeneous LC phase is observed (Fig. 5b). On further polymerization (beyond t_r = 180 s) the LC phase transforms into the crystalline phase.

The effect of reaction temperature and composition on the LC layer formation and early precipitation in the 2,5-FDCA/DABP/ABA systems was determined, and is shown in a phase diagram as a function of ABA content (Fig. 6). Region *I* in Fig. 6 indicates the regime where a full dissolution and reaction of the 2,5-FDCA monomers occurs, while region *II* indicates the regime where crystallization occurs prior to the full reaction of the 2,5-FDCA monomers. Generally, the reaction temperature required to reach full conversion increases with the increasing 2,5-FDCA concentration to a maximum of 330 °C for systems having 41 mol% or higher amounts of 2,5-FDCA. Apparently, the reaction temperature of 330 °C lies close enough to the melting temperature of 2,5-FDCA of 342 °C to allow rapid dissolution and reaction [46].

Interestingly, the 2,5-FDCA/DABP/ABA system shows LC behavior along the whole range of compositions. However, the temperature required to observe the LC phase increases steadily from 200 to 210 °C for pure POBA to 340 °C for 2,5-FDCA/DABP/ABA 40/40/20 systems. Above this temperature, the LC phase is observed, but if the reaction temperature is too low, crystallization from the isotropic melt occurs. For example, for the 2,5-FDCA/DABP 50/50 system, the LC phase is only observed above 360 °C.

In the discussion of the data obtained thus far via the TFP, we have neglected the effect of the thermal instability of the 2,5-FDCA monomer on the polymerization. According to the data obtained by Gruter [39] and Drewitt [40], it should be realized that the

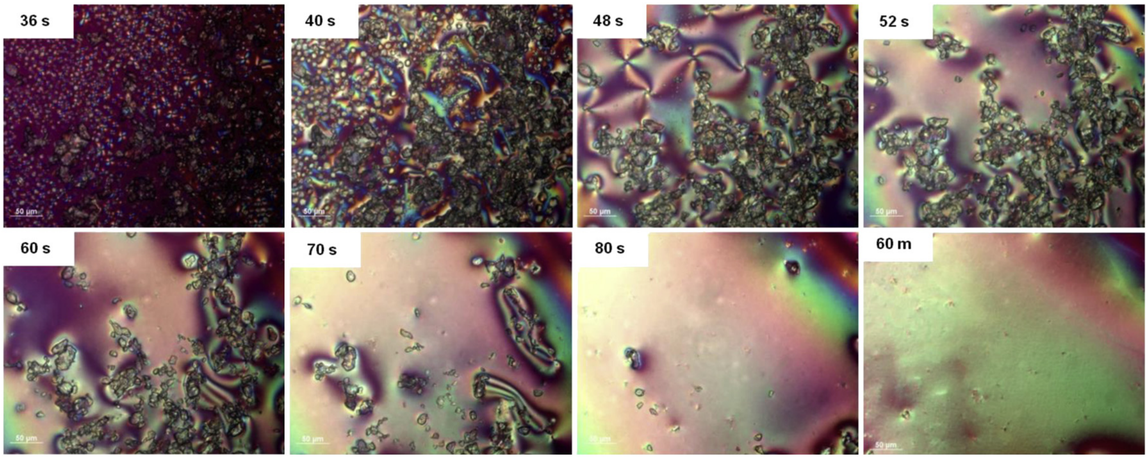

Fig. 7. Optical micrographs showing formation of a stable LC melt in a TFP of the 2,5-FDCA/DABP/ABA/AVA 15/15/60/10 reaction system at 300 °C.

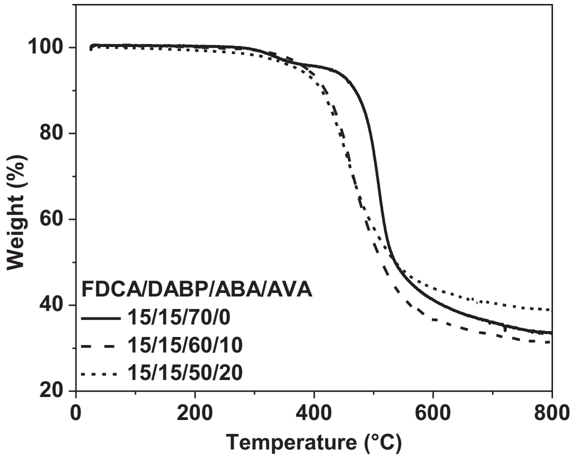

Fig. 8. TGA thermograms showing a decrease of the weight loss temperature with the incorporation of AVA in 2,5-FDCA/DABP/ABA/AVA 15/15/70/0, 15/15/60/10 and 15/15/50/20 polymers synthesized via the TFP route at 300 °C.

maximum polymerization temperature of 2,5-FDCA is 280 °C or lower, since severe discoloration occurs at 280 °C or higher. Preferably, reactions containing 2,5-FDCA should be conducted below 220 °C to fully prevent any side reaction. According to Fig. 6, only the 2,5-FDCA/DABP/ABA systems with ~30 mol% 2,5-FDCA or less can be successfully synthesized at 280 °C or below, without having the reaction mixture crystallizing prior to the full dissolution of the 2,5-FDCA monomers.

3.2. *Tuning the melting temperature of 2,5-FDCA based polymers*

Since the high melting temperatures of the 2,5-FDCA/DABP/ABA polymers do not allow molecular weight build-up, mainly due to rapid crystallization from the melt, O-acetylvanillic acid (AVA) has been used as a co-monomer during polymerization. It was anticipated that the presence of the methoxy group of AVA perturbs the crystal lattice of the 2,5-FDCA/DABP/ABA systems and lowers the melting temperature. A small fraction of ABA was replaced by AVA to determine the influence of AVA on the melting temperature. These systems were investigated using the TFP. It is conclusively demonstrated that on fixing the 2,5-FDCA/DABP content to 30 mol% and by varying the amount of AVA between 0 and 20 mol% a series of polymers having thermotropic LC behavior can be obtained. Fig. 7 shows an example of the morphological changes observed in the 2,5-FDCA/DABP/ABA/AVA 15/15/60/10 copolymer at 300 °C. The formation of the LC phase occurs prior to the complete dissolution of the 2,5-FDCA crystals. These observations are similar to the 2,5-FDCA/DABP/ABA 15/15/70 system, where in the initial stages of polymerization 2,5-FDCA monomers are not distributed randomly along the polymer chains. To recall, in the 2,5-FDCA/DABP/ABA 15/15/70 system, the distribution of the monomers along the main-chain is thought to be of a blocky nature due to rapid crystallization of the polymer chains during polymerization, preventing transesterification. However, in the 2,5-FDCA/DABP/ABA/AVA 15/15/60/10 copolymer the absence of crystallization during polymerization allows for the transesterification in the melt, promoting a random distribution of the monomers along the chain and inhibiting the block formation.

In Fig. 7, with the increasing polymerization time, the LC drops coalesce rapidly and a typical Schlieren texture is formed while the 2,5-FDCA monomer dissolves and reacts. The LC phase is observed after 2 min of reaction time in full view of the optical micrograph. The LC melt does not show any phase transition within 60 min of reaction time and remains in the mobile melt phase. The absence of crystallization allows for build-up of molecular weight by transesterification in the LC melt. Upon cooling at 10 °C/min, solidification of the sample is observed at 230–240 °C (T_c), while upon heating at 10 °C/min again, the crystal to LC transition is observed around 270–280 °C (T_m). Similar experiments are performed with the 2,5-FDCA/DABP/ABA/AVA 15/15/50/20 system, at different reaction temperatures, showing the formation of a homogeneous LC phase and no crystallization until 120 min of reaction time. The system shows crystallization at 200 °C upon cooling at 10 °C/min and on heating shows the transition from the crystalline to the LC phase at 240 °C. This data clearly indicates that AVA decreases the melting temperature of the 2,5-FDCA/DABP/ABA systems and provides opportunities for increasing the molecular weight in the LC phase at temperatures below 300 °C.

The thermal stability of the 2,5-FDCA15/DABP15/ABA/AVA polymers with 0% AVA, 10% AVA and 20% AVA, synthesized through

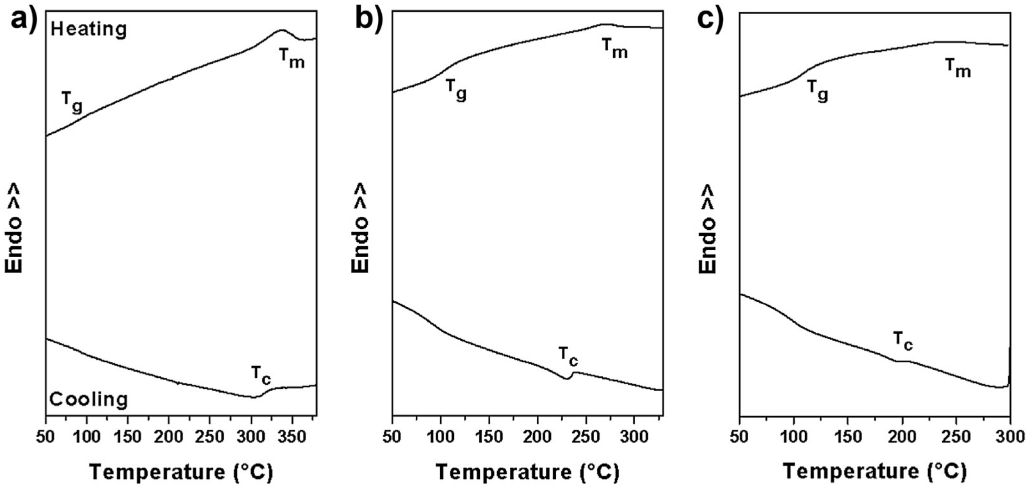

Fig. 9. Second heating and cooling DSC traces showing the decrease of the melting temperature with the increasing amount of AVA in the 2,5-FDCA/DABP/ABA/AVA a) 15/15/70/0, b) 15/15/60/10 and c) 15/15/50/20 TFP systems synthesized at 300 °C.

Table 1
Thermal data showing the influence of AVA on the T_g, T_m, ΔH_{melt} and T_{ons} of polymers obtained from 2,5-FDCA/DABP/ABA/AVA systems.

AVA content	T_g[a] (°C)	T_m[a] (°C)	ΔH_{melt}[a] (J/g)	T_m[b] (°C)	T_{ons}[c] (°C)
0 mol%	96.7	336.6	6.80	360–380	460
10 mol%	103.5	275.3	1.77	270–280	411
20 mol%	109.2	230.3	0.66	240–250	402

[a] Obtained from the second heating runs in DSC experiments during heating and cooling at a rate of 10 °C/min.
[b] Obtained from optical microscopy experiments during heating and cooling at a rate of 10 °C/min.
[c] Obtained from TGA experiments with a heating rate of 20 °C/min.

TFP at 300 °C, is evaluated by TGA and the thermograms are shown in Fig. 8. The 2,5-FDCA/DABP/ABA 15/15/70 system shows an onset of weight loss (T_{ons}) at 475 °C, but partial weight loss of 5 wt% occurs around 350–370 °C. The partial weight loss of the polymer is likely to be a result of the limited thermal stability of the low molar mass component of the polymer that crystallizes during polymerization. The introduction of AVA into the 2,5-FDCA/DABP/ABA copolymer decreases the onset temperature for thermal degradation from 475 °C to 411 °C. Furthermore, the polymers showed no weight loss for at least 1 h at the isothermal temperature of 300 °C as observed by TGA.

DSC analysis of the different 2,5-FDCA/DABP/ABA/AVA systems synthesized using the TFP at 300 °C is performed and the information obtained from the second heating runs is depicted in Fig. 9. It should be noted that the peak melting temperature (T_m) of the first heating run of the 2,5-FDCA/DABP/ABA/AVA 15/15/70/0 system is observed at 369 °C in the first heating run, but shifts to 330 °C during the second heating run. This shift is expected to be a result of the partial degradation, as observed in the TGA analysis. However, also the transesterification occurring upon melting of the sample in the DSC can lower the melting temperature observed in the second heating run. From the data shown in Fig. 9, it is evident that the addition of AVA lowers the peak melting temperature of the polymers, causes a broadening of the melting endotherm, and decreases the melt-enthalpy (ΔH_{melt}). The glass transition temperatures (T_g) of the copolymers containing AVA become more pronounced and shift to higher temperatures with the increasing content of vanillic acid, Table 1. The increase of the T_g is likely to arise because of the methoxy groups along the polymer backbone that limit the rotational motion of the aromatic rings along the chains.

4. Conclusions

The thin-film polymerization is employed to successfully study the 2,5-FDCA incorporation in aromatic thermotropic polyesters. The 2,5-FDCA monomer shows a limited solubility and reactivity behavior in the melt, similar to terephthalic acid. The limited solubility requires extended reaction times or increased reaction temperatures to successfully dissolve the 2,5-FDCA monomer and incorporate it into the polymer backbone. However, the thermal stability of 2,5-FDCA limits the reaction temperature and reaction temperatures well below 300 °C are preferred. The copolymerization of AVA successfully decreases the melting temperature and indicates that there is a window for the synthesis of polymers containing 2,5-FDCA in a melt-polycondensation temperatures below 300 °C. The screening method adopted here has been helpful in identifying the monomer mixtures and reaction conditions that have been successfully adapted for up-scaling of the process to 100 g scale. The polymer synthesis and properties of the up-scaled materials will be a part of future publications.

Acknowledgment

This work is part of the research program of the Dutch Polymer Institute (DPI), #739 BioLCP. The authors acknowledge financial support by Teijin Aramid, The Netherlands at the initial stage of this project.

Abbreviations

ABA	*p*-acetoxybenzoic acid
AVA	4-acetoxy-3-methoxybenzoic acid or O-acetylvanillic acid
BP	4,4′-biphenol
DABP	4,4′-diacetoxybiphenyl
2,5-FDCA	2,5-furandicarboxylic acid
HBA	*p*-hydroxybenzoic acid or 4-hydroxybenzoic acid
ΔH_{melt}	melt-enthalpy
POBA	poly(oxybenzoic acid)
LC	liquid crystalline
TA	terephthalic acid
TFP	thin-film polymerization
T_g	glass transition temperature
TLCP	Thermotropic Liquid Crystalline Polyesters
T_r	reaction temperature
T_m	peak melting temperature (DSC) or crystal to liquid crystal transition (POM)

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