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

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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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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.

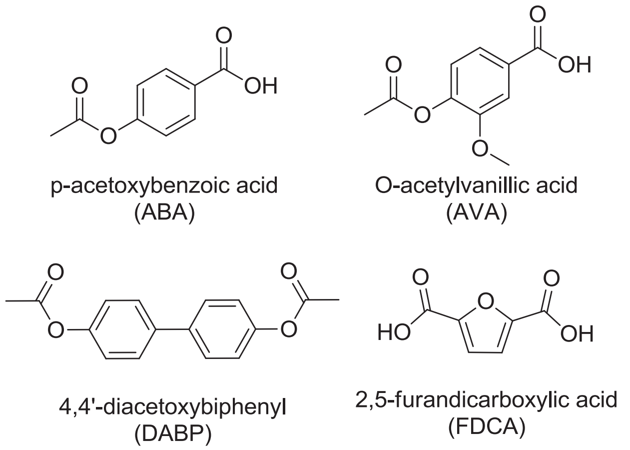
p-acetoxybenzoic acid (ABA)
O-acetylvanillic acid (AVA)
4,4'-diacetoxybiphenyl (DABP)
2,5-furandicarboxylic acid (FDCA)

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).