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Processing and performance of aromatic-aliphatic thermotropic polyesters based on vanillic acid

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ABSTRACT

In this work we report on the processing, melt-drawing, and performance of new vanillic acid based aliphatic-aromatic thermotropic polyesters. It is demonstrated that these materials are easily processed from their nematic melts yielding highly oriented products. Furthermore, we demonstrate that a molecular weight (M_w) of roughly 30 kg/mol is required in order to successfully perform spinning on these polymers. The application of a polymer with lower M_w results in poor mechanical performance and fiber breakage during the winding process. Wide-angle X-ray diffraction analysis has been performed on the fibers and it is demonstrated that the orientation parameter increases with increasing draw-ratio of the fiber. Although these polymers are readily processed from their thermotropic melts, the obtained fibers only retain their orientation up to temperatures in the range of 120–130 °C, after which they start to melt. In general, these fibers exhibit tensile moduli in the range of ~10 GPa and a tensile strength around ~150–200 MPa. FTIR and solid-state NMR experiments indicate that only the aromatic components are molecularly oriented during the spinning process. In contrast, the aliphatic moieties exhibit a high mobility, normally corresponding to a local isotropic motion. It is expected that the poor molecular orientation of the aliphatic moieties in these aliphatic-aromatic thermotropic polyesters contribute to the relatively low tensile modulus of the fibers, obtained after the extrusion and melt-drawing process.

1. Introduction

The synthesis, processing and performance of thermotropic polyesters have widely been investigated over the last decades. Their low melt-viscosity, the ease in processing and the highly anisotropic products obtained after melt-processing have resulted in numerous publications and commercialization of different thermotropic polyesters [1–8]. Perhaps the most widely used thermotropic polyesters are the *p*-hydroxybenzoic acid (BA) and 6-hydroxy-2-naphthoic acid (NA) based copolymers, commercially known as the Vectra® series. Generally, fibers spun from the Vectra® polymer series (Vectran® fibers), have tensile moduli around 50 GPa and tensile strengths of over 1 GPa after processing from their thermotropic melt. Additionally, heat treatment of these fibers increases their mechanical performance, yielding fibers with tensile moduli ~100 GPa and tensile strengths around 3–4 GPa. Generally, the increase in tensile modulus upon heat-treatment is attributed to the reorganization of the monomer sequences resulting in the formation of bigger and more perfect crystals. The improved tenacity of the fibers after heat-treatment is attributed to the occurrence of a post-condensation reaction, resulting in an increase of the molecular weight which facilitates a better stress transfer along the polymer chains [9].

From this data it becomes clear that heat-treatment is essential for semi-crystalline fully aromatic thermotropic polyester fibers, to achieve the best mechanical performance. However, the application of such a heat-treatment is only possible when the obtained fiber is dimensionally stable at the applied annealing temperatures,

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commonly in the range of 250–300 °C. For example, the application of such a heat-treatment is not possible for amorphous thermotropic polyesters or for thermotropic polyesters that have too low melting temperatures. An example of an amorphous fully aromatic thermotropic polyester, based on terephthalic acid, NA, and 4,4′-dihydroxy-2,2′-dimethyl-biphenyl, has been reported by Grasser and coworkers [10]. Although these polymers exhibited no melting or crystallization transition, fiber spinning from the thermotropic melt yielded fibers with tensile modulus in the range of 50 GPa and a tensile strength of approximately 0.5 GPa.

A well-known example of aliphatic-aromatic thermotropic polyesters is the copolymer of poly(ethylene terephthalate) (PET) and BA. Depending on the processing temperature, processing of these copolymers with 60 mol% BA from the thermotropic melt yields fibers having tensile moduli between 10 and 30 GPa [11,12]. Another example of thermotropic fibers spun from aliphatic-aromatic polymers has been reported by Dingemans and coworkers [13]. These authors reported the synthesis and preliminary fiber spinning results of polymers containing flexible suberic acid and sebacic acid spacers. The obtained fibers exhibit a tensile modulus of 15 GPa and a tensile strength of 0.12 GPa. Although the presence of these aliphatic spacers drastically decreases the tensile performance of the obtained fibers, it is clear that fibers with promising tensile moduli can still be obtained. Besides, these aliphatic spacers drastically decrease the melting and processing temperatures of thermotropic polymers, and allow for the incorporation of monomers that are thermally instable at high temperatures.

In previous publications, we have reported routes to successfully design thermotropic polyesters based on vanillic acid (Fig. 1) [14,15]. In these publications we demonstrated that the synthesis of high molecular weight copolymers containing small amounts of vanillic acid could be performed at low temperatures from the melt, generally yielding polymers with melting temperatures close to or below 200 °C. Furthermore, the presence of vanillic acid is known to (a) improve the monomer sequence distribution, (b) increase the stability of the thermotropic melt, (c) decrease the polymer melting temperature, and (d) improve the spinnability of thermotropic polyesters [15–18]. To be more specific and relevant for the polymers investigated in this publication (Fig. 1) is that the presence of vanillic acid results in a crystal to nematic (K–N) phase transition close to 150 °C. No nematic to isotropic (N–I) transition was observed prior to degradation. Thus the preferred processing window for these polymers exists above 150 °C. Although the benefits of the copolymerization of vanillic acid are interesting from a chemical viewpoint, the low melting temperature of the polymers limits the application of these polymers at high temperature and might not allow for the processed products to undergo a heat-treatment step. These factors, mainly resulting from the presence of the aliphatic spacers, might limit the application of these fibers for practical purposes.

In this manuscript we evaluate the effect of different processing routes on the mechanical performance of vanillic acid based renewable aliphatic-aromatic thermotropic polyesters having different molecular weights. The used processing conditions are fiber spinning, compression molding, and solvent casting. Differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), wide-angle x-ray diffraction (WAXD), polarization optical microscopy (POM), Fourier-Transform Infra-Red (FTIR), and solid-state NMR spectroscopy are used to characterize the processed products. Special attention is paid to the thermal behavior, orientation and mechanical performance of the processed products and possibilities to perform heat-treatment steps are investigated.

2. Experimental section

2.1. General polymerization procedure

Thermotropic polyesters containing *p*-hydroxybenzoic acid (HBA), vanillic acid (VA), suberic acid (SuA), and hydroquinone (HQ) were prepared using a 200 g scale acidolysis melt-polycondensation reaction. The monomers were loaded into a 500 mL three-neck round bottom flask fitted with a mechanical stirrer, together with 50–100 mg of $Zn(AcO)_2$ and the temperature was gradually increased to 260 °C. Acetic acid was distilled off and reduced pressure was applied to the system for eight to twelve hours after roughly 90% of the expected acetic acid was collected. Details regarding the polymerization procedure are reported in a previous publication [15].

2.2. Processing of thermotropic polyesters

Solvent cast films of the polymers used in this study were prepared via dissolution of polymer samples in a 2:1 mixture (v/v) of chloroform/1,1,1,3,3,3-hexafluoroisopropanol ($CHCl_3$/HFIP) at room temperature. The concentrations of the casting solutions were 1 g polymer per 3 mL solvent. Once the polymers were fully dissolved, the casting solutions were poured onto an aluminum plate and the films were allowed to dry at room temperature for 3 h followed by drying *in vacuo* at 40 °C overnight. The obtained polymer films were slightly yellow/brown and transparent. To ensure the full removal of any residual solvent, heat treatment and thorough drying of the samples was performed in a second drying step above T_g at 80 °C.

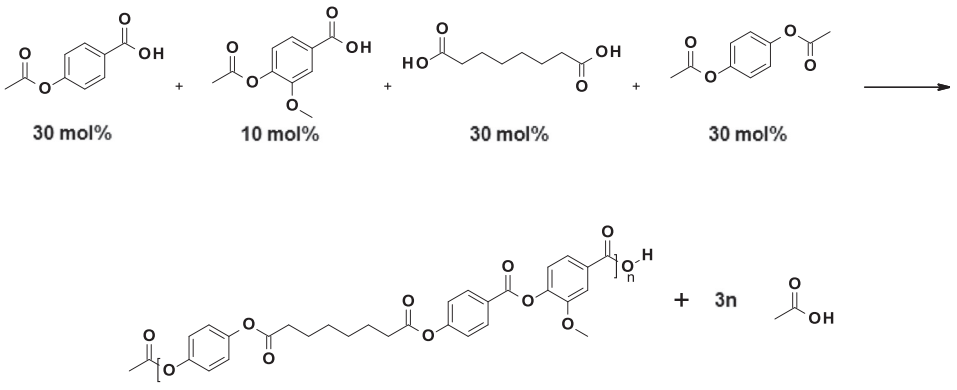

Fig. 1. Acidolysis reaction and composition of polymers **I**–**III** synthesized in this study. *N.b.* the resulting polymer is a copolymer.