# Macromolecules

# Melt Derived Blocky Copolyesters: New Design Features for Polycondensation

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**Supporting Information** 

**ABSTRACT:** Melt polycondensation was utilized to chain extend polytrimethylene terephthalate with 1,3-propanediol based fluorinated isophthalic oligomers, resulting in copolymers with retained microstructure. Our findings point toward the formation of a blocky type copolymer. In general, formation of block or segmented copolymers from melt derived polycondensation is a very challenging task due to the propensity for adverse randomization reactions. Supported by size exclusion chromatography, our copolymers are fully chain extended, with no presence of the initial components. Furthermore, thermal differential scanning calorimetry has



confirmed that the melt characteristics of the starting components are retained. In addition, interaction polymer chromatography and sequence distribution analysis using <sup>13</sup>C NMR supports a blocky backbone microstructure. Seemingly, intermolecular chain end condensation occurs, whereas transesterification is dormant. While these findings open up new doors for polymer/materials development, we are particularly interested in these structures as melt additives to address oil repellency of polyester blends. When used in blends these blocky additives show an improvement in oil repellency compared with random additives of identical molar composition, i.e., they are more fluorine efficient.

# ■ INTRODUCTION

Fluorinated man-made materials have provided consumer benefits for a wide range of applications during the last 50 years. Fluorinated molecules, for example, constitute the primary component in refrigerants, and fluorinated polymers are used in a vast array of products including textiles, carpets, cookware, pipes/tubes, construction materials, and electronic materials to provide, for example, repellency, lubricity, chemical inertness, and low dielectric constant materials.<sup>1</sup> In polymers, the utilization of fluorine can be separated into three main categories: (i) polytetrafluoroethylene (PTFE), (ii) melt processable fluorinated (co)polymers including fluorinated ethylene propylene (FEP), perfluoroalkoxys (PFA), and Krytox, (iii) tetrafluoroethylene telomers. While these classes of fluorinated materials provide specific benefits for the application, they share a common feature in being derived from radical chain growth polymerization (except for Krytox that is made from ring-opening polymerization of hexafluoropropylene oxide). We have recently modified fluorinated monomers available for chain growth polymerization to be compatible for step growth polycondensation, thus opening the scope to a new range of industrially relevant polymers including polyesters, polyamides, and polyaramids. The essence of this finding was the preparation of fluorinated aromatic ethers, via the addition of hydroxyl aromatic diesters to fluorinated vinyl ethers, under base catalyzed conditions.<sup>2</sup> The reaction is mild, efficient, and scalable, and the obtained monomer is compatible with standard polycondensation protocols. Furthermore, this

new line of building blocks fills a shortcoming of fluorinated monomers available for step growth polymerization, and importantly allows pendant trifluoromethyl functional groups to be readily introduced to polymers. Trifluoromethyl is a very useful functional group, known to provide even lower surface tension than PTFE.<sup>1,3</sup> When used in polyesters, polyamides, and polyaramids, the resulting fluorinated (co)polymers were found to possess increased repellency to water and oil.<sup>4–6</sup> We have recently built on the synthetic design capability of these materials to prepare blocky fluorinated/nonfluorinated aromatic copolyesters derived from a commercially attractive melt process, a feature not typical for polycondensation polymers.

As background, Wallace Carother's pioneering research on step growth polycondensation was the onset for the development of engineering polymers in the 20th century.<sup>7,8</sup> Whereas Carothers and co-workers outlined synthetic routes to polyesters, polyamides, and others, Flory later coupled experimental observations to theoretical considerations. Indeed, one of the fundamental features of polycondensation is that of equal reactivity between functional groups at all stages of the polymerization.<sup>9</sup> There are several implications. For one, it is difficult to control the molecular weight or the molecular weight distribution of the formed polymer (PDI ~ 2.0 for a polycondensation process). This can be understood by the fact

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that monomers, without discrimination, readily react with other monomers, oligomers, or polymers. Another implication of equal reactivity is that a selected molecular structure, e.g., sequences of specific monomer units along the chain, is hard to achieve. If one, for example, would polymerize isophthalic and terephthalic acid in equal proportions together with one particular glycol, for example ethylene glycol, this would render a random copolymer structure in which isophthalate and terephthalate units would randomly appear along the polymer backbone. Published data reports that all crystallinity seen in PET is removed by replacing ~20% of terephthalic acid with isophthalic acid, i.e. a fully amorphous copolymer is formed.<sup>10</sup> Similar results are found if one would target a 50/50 mol % incorporation of two different glycols, for example ethylene glycol and 1,3-propanediol, in combination with dimethylterephthalate; this too renders a dominantly amorphous copolymer.<sup>11</sup> As most commodity polycondensation polymers are homopolymers from the same set of diol/diamine and diacid, for example nylon-6,6, poly(ethylene terephthalate), and poly(butylene terephthalate), this feature perhaps is of less concern. However it does construct a major hurdle if one would consider the manufacturing of structurally challenging compositions like segmented or block copolymers, based solely on a polycondensation process. The literature entails numerous examples of the use of disparate polymerization techniques to provide block copolymers. A chain growth polymerization technique could be used followed by a step growth polymerization to render a blocky type copolymer, or vice versa. One example is the Hytrel thermoplastic elastomer which consists of a soft poly(tetramethylene glycol) segment made from ringopening polymerization of tetrahydrofuran and a hard poly-(butylene terephthalate) segment prepared through step growth polymerization.<sup>12</sup> Similarly, fluorinated elastomers were introduced by Tonelli et al.<sup>13</sup> Another noteworthy achievement is the work by Yokozawa et al. They have developed a so-called chain growth polycondensation process for the manufacturing of condensation polymers with defined molecular weights, narrow molecular weight distributions and selective compositions.<sup>14,15</sup> It is achieved by the incorporation of monomers with substituents of various electron donating ability, such that the monomer-monomer reactivity is suppressed and that monomers instead selectively add to propagating polymer chain-ends. This leads to a living polycondensation process in which controlled molecular weights and narrow polydispersities (i.e., PDI's below 1.2) are achieved. Furthermore, it allows one to add monomers in sequence for the construction of block copolymers, star- and graft polymers.

In this report we outline new and selective routes to blocky copolyesters utilizing polycondensation entirely in the melt. This is demonstrated using polytrimethylene terephthalate (PTT) and oligomers based on novel fluorinated aromatic ether monomers. This new family of fluorinated monomers provides the ability to address oil repellency of inherently lipophilic aromatic polyesters, like PTT, and others, while at the same time introducing new macromolecular design capabilities.

#### EXPERIMENTAL SECTION

**Materials.** Purchased from Aldrich Chemical Co., and used as received, were: dimethyl terephthalate, titanium(IV) isopropoxide (TyzorTPT), tetrahydrofuran, dimethyl 5-hydroxyisophthalate, potassium carbonate. Obtained from the DuPont Company and used as received, unless otherwise noted, were: Biobased 1,3-propanediol (Bio-

PDO) [1,3-propanediol used in polyesters aka 3G], 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2-trifluorovinyloxy) propane (PPVE), Poly-(trimethylene terephthalate) (PTT aka 3-GT), bright 1.02 IV ( $M_n$  25800 g/mol,  $M_w$  49700, PDI 1.92, DP ~ 125). Purchased from SynQuest Laboratories, and used as received: 1,1,1,2,2,3,3-heptafluoro-3-(1,1,1,2,3,3-hexafluoro-3-(1,2,2-trifluorovinyloxy)propan-2-yloxy)-propane (PPPVE).

**Methods.** Surface Analysis. The purpose of the analysis was to study various blends and functional polymers ability to repel hexadecane (oil) and to measure surface tensions. Surface contact angles of hexadecane (advancing and receding) on polymer film were recorded on a Ramé-Hart Model 100–25-A goniometer (Ramé-Hart Instrument Co) with an integrated DROPimage Advanced v2.3 software system. Four  $\mu$ L of hexadecane was dispensed using a micro syringe dispensing system. Surface tensions were calculated using the mean-harmonic method utilizing methyl iodide and water as probe liquids.<sup>26</sup>

Size Exclusion Chromatography. A size exclusion chromatography system Alliance 2695 from Waters Corporation (Milford, MA), was provided with a Waters 414 differential refractive index detector, a multiangle light scattering photometer DAWN Heleos II (Wyatt Technologies, Santa Barbara, CA), and a ViscoStar differential capillary viscometer detector (Wyatt). The software for data acquisition and reduction was Astra version 5.4 by Wyatt. The columns used were two Shodex GPC HFIP-806 Mstyrene-divinyl benzene columns; and one Shodex GPC HFIP-804 Mstyrene-divinyl benzene column. The specimen was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) containing 0.01 M sodium trifluoroacetate by mixing at 50 °C with moderate agitation for 4 h followed by filtration through a 0.45  $\mu$ m PTFE filter. Concentration of the solution was 2 mg/mL. Data was taken with the chromatograph set at 35  $^\circ$ C, with a flow rate of 0.5 mL/ min. The injection volume was 100  $\mu$ L. The run time was 80 min. Data reduction was performed incorporating data from all three detectors described above. Eight scattering angles were employed with the light scattering detector. No standard for column calibration was involved in the data processing

Interaction Polymer Chromatography. The purpose of interaction polymer chromatography was to separate macromolecules based on functionality. The experiments were performed using chromatography system Alliance 2695 coupled with UV/vis 287 detector from Waters at a 290 nm wavelength. FluoroFlash F8 HPLC  $4.6 \times 150$  mm column from Fluorous Technologies (PA, USA) has been used for separation in linear water-HFIP (65–100%) 20 min gradient at flow rate 0.5 mL/min.

Thermal Analysis. Glass transition temperature  $(T_g)$  and melting point  $(T_m)$  were determined by differential scanning calorimetry (DSC) performed according to ASTM D3418–08. Specifically a heat–cool–heat protocol was used, under a protecting nitrogen atmosphere, that heated (from 0 to 250 °C), cooled (from 250 to 0 °C), and reheated (from 0 to 250 °C) samples at 10°/min, and thermal transitions were recorded.

*NMR Analysis.* <sup>13</sup>C NMR data was acquired on a 700 MHz NMR Varian direct drive with a 10 mm probe, on 310 mg of polymer and 30 mg of chromium acetyl acetonate (CrAcAc) dissolved in deuterated 1,1,2,2 tetrachloroethylene (tce-d2) to 3.1 mL total volume with minimal heating. Specifically only the CH<sub>2</sub>O ester carbon was analyzed for sequence distribution determination. Four CH<sub>2</sub>O ester carbons were analyzed in the region of 62.6–62.0 ppm of the copolymers made and <sup>13</sup>C NMR data is only given for those compositions. NMR spectra were acquired using an acquisition time of 1 s, 90 deg pulse of about 11  $\mu$ s, spectral width of 44.6 kHz, recycle delay of 5 s, temperature of 120 °C, 2500–4500 transients averaged. Data processed typically with exponential line broadening of 0.5–2 Hz and zero fill of 512k. Spectra were referenced to the tce-*d*<sub>2</sub> carbon at 74.2 ppm.

Blends of PTT and Fluorinated Additives Using a DSM Microcompounder. Blends of neat PTT with fluorinated homo or copolymers were made in a DSM microcompounder. In general, blends were made with copolymer additives targeting a total additive concentration of  $\sim 1-50$  wt %. The DSM system is a PC controlled 15 cubic centimeter (cc), co-rotating, intermeshing (self-wiping), 2-

tipped, conical twin-screw machine with a recirculation loop, discharge valve, nitrogen purge system, and with three different heating zones. Typically, a temperature of 250 °C was used for all three heat zones. Under nitrogen, PTT and the additive were charged and stirred with a speed of 150 rpm for a total mixing time of 5 min. The stirring speed and mixing may be varied, for example, speeds of 245 rpm with 5 min mixing time could alternatively be used. Following the given mixing time the discharge valve was opened and an extruded ribbon collected.

Synthesis of Dimethyl 5-(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy) Isophthalate ( $F_{10}$ -iso). In a nitrogen gas supplied drybox, anhydrous THF (500 mL) and dimethyl 5-hydroxy-isophthalate (42 g, 0.20 mol) were added to an oven dry 1000 mL round-bottom flask equipped with a stir bar. Potassium carbonate (6.9 g, 50.4 mmol) was added and an addition funnel connected. 1,1,1,2,2,3,3-Heptafluoro-3-(1,2,2-trifluorovinyloxy)propane (79.80 g, 0.30 mol) was added via the addition funnel and the reaction mixture was heated to reflux and stirred overnight ( $t \sim 16$  h), oil bath temperature ~80 °C. The following morning the potassium carbonate catalyst was removed via filtration through a bed of silica gel. The supernatant was concentrated under vacuum (roto-vap) and then vacuum distilled, collecting the fraction boiling at 139–145 °C (1.8–1.5 Torr), yielding 81.04 g (85%) of a clear liquid product. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.60 (s, 1H), 8.03 (s, 2H), 6.22 (d, 1H), 3.95 (s, 6H).

Synthesis of (Dimethyl 5-(1,1,2-trifluoro-2-(1,1,2,3,3,3-hexafluoro-2-(perfluoropropoxy)propoxy)ethoxy) Isophthalate (F<sub>16</sub>-iso). In a nitrogen gas supplied drybox, anhydrous THF (500 mL) and dimethyl 5-hydroxy-isophthalate (42 g, 0.20 mol) were added to an oven dry 1000 mL round-bottom flask equipped with a stir bar. Potassium carbonate (6.95 g, 50.4 mmol) was added and an additional funnel connected. 1,1,1,2,2,3,3-Heptafluoro-3-(1,1,1,2,3,3-hexafluoro-3-(1,2,2-trifluorovinyloxy)propan-2-yloxy)propane (129.60 g, 0.30 mol) was added via the addition funnel and the reaction mixture was heated to reflux and stirred overnight (t~16hrs), oil bath temperature ~80 °C. The following morning the potassium carbonate catalyst was removed via filtration through a bed of silica gel. The supernatant was concentrated under vacuum (roto-vap) and then vacuum distilled, collecting the fraction boiling at 141-148 °C (1.1-0.95 Torr), yielding 123.3 g (96%) of a clear liquid product. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 8.60 (s, 1H), 8.03 (s, 2H), 6.22 (d, 1H), 3.95 (s, 6H).

Preparation of 3-GF<sub>10</sub>-iso Homopolymer from F<sub>10</sub>-iso and 1,3-Propanediol. A 150 g sample of the  $F_{10}$ -iso prepared and 43.1 g of 1,3propanediol were charged to an oven-dried 500 mL three necked round-bottom flask equipped with an overhead stirrer and a distillation condenser kept at 23 °C. The reactants were stirred under a nitrogen purge at a speed of 50 rpm. The contents were degassed three times by evacuating down to 100 Torr and refilling back to atmospheric pressure with N<sub>2</sub> gas. TyzorTPT catalyst (45 mg) was added after the first evacuation. The flask was then immersed into a preheated metal bath set at 160 °C and held for 20 min while slowly increasing the stirring speed to 180 rpm after which the temperature was increased to 210 °C and the reaction flask was held for an additional 90 min still at 180 rpm. Following the 90 min hold, the nitrogen purge was discontinued and a vacuum ramp was started such that after about 60 min the vacuum reached a value of 50-60 mTorr. The reaction was held for an additional 90 min with stirring at 180 rpm. The heat source was then removed. The overhead stirrer was then stopped and elevated from the floor of the reaction vessel. The vacuum was then turned off, and the system was purged with N2 gas. The thus formed product was allowed to cool to ambient temperature. The product was recovered after carefully breaking the glass with a hammer. Yield =

<sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.60 (ArH, s, 1H), 8.00 (ArH–, s, 2H), 7.70 (ArH, s, 4H), 6.15 (-CF<sub>2</sub>-CFH–O–, d, 1H), 4.70–4.50 (COO–CH<sub>2</sub>–, m, 4H), 3.95 (-CH<sub>2</sub>–OH, t, 2H), 3.85 (-CH<sub>2</sub>–O–CH<sub>2</sub>–, t, 4H), 2.45–2.30 (-CH<sub>2</sub>–, m, 2H), 2.10 (-CH<sub>2</sub>–CH<sub>2</sub>–O–CH<sub>2</sub>–, CH<sub>2</sub>–, m, 4H).

Preparation of 3-GF<sub>16</sub>-iso Homopolymer from  $F_{16}$ -iso and 1,3-Propanediol. A 150 g sample of the  $F_{16}$ -iso prepared and 32 g of 1,3propanediol were charged to an oven-dried 500 mL three necked round-bottom flask equipped with an overhead stirrer and a distillation condenser. The reactants were stirred under a nitrogen purge at a speed of 50 rpm while the condenser was kept at 23 °C. The contents were degassed three times by evacuating down to a pressure of 100 Torr and refilling back to atmospheric pressure with N<sub>2</sub> gas. TyzorTPT catalyst (45 mg) was added after the first evacuation. The flask was immersed into a preheated metal bath after the three degassing/repressurization cycles set at 210  $^\circ\text{C}$  and held for 90 min while stirring speed was increased from 50 to 180 rpm. Following the 90 min hold, the nitrogen purge was discontinued and a vacuum ramp was started such that after about 60 min the vacuum reached a value of 50-60 mTorr. The reaction was held under vacuum at 50-60 mTorr for an additional 90 min with stirring at 180 rpm. The reaction vessel was then removed from the heat source. The overhead stirrer was stopped and elevated from the floor of the reaction vessel. The vacuum was then turned off and the system was purged with N2 gas at atmospheric pressure. The thus formed product mixture was allowed to cool to ambient temperature. The product was recovered after carefully breaking the glass with a hammer. Yield = 88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 8.60 (ArH, s, 1H), 8.00 (ArH-, s, 2H), 7.70 (ArH, s, 4H), 6.15 (-CF<sub>2</sub>-CFH-O-, d, 1H), 4.70-4.50 (COO-CH<sub>2</sub>-, m, 4H), 3.95 (-CH<sub>2</sub>-OH, t, 2H), 3.85 (-CH<sub>2</sub>-O-CH<sub>2</sub>-, t, 4H), 2.45-2.30 (-CH<sub>2</sub>-, m, 2H), 2.10 (-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-, m, 4H).

Preparation of PTT Homopolymer from Dimethylterephthalate and 1,3-Propanediol. Dimethylterephthalate (150 g), and 1,3propanediol (105.9 g) were charged to an oven-dried 500 mL three necked round-bottom flask equipped with an overhead stirrer and a distillation condenser. The reactants were stirred under a nitrogen purge at a speed of 10 rpm while the condenser was kept at 23 °C. The contents of the flask were degassed three times by evacuating down to 500 mTorr and refilling back to atmospheric pressure with N<sub>2</sub> gas. TyzorTPT catalyst (94 mg) was added after the first evacuation. Following the three degassing cycles, the flask was immersed into a preheated metal bath set at 160 °C. The solids were allowed to completely melt at 160 °C for 20 min while the stirring speed was slowly increased to 180 rpm. The temperature was increased to 210  $^\circ\mathrm{C}$ and was held at 210 °C for 90 min. After 90 min at 210 °C, the temperature was increased to 250 °C after which the nitrogen purge was discontinued, and a vacuum ramp was started such that after about 60 min the vacuum reached a value of about 60 mTorr. After an additional 30 min at 250 °C and 60 mTorr, the heat source was removed. The overhead stirrer was stopped and elevated from the floor of the reaction vessel. The vacuum was then turned off and the system purged with N2 gas at atmospheric pressure. The thus formed product was allowed to cool to ambient temperature. The product was recovered after carefully breaking the glass with a hammer. Yield = 85% of PTT polymer. <sup>1</sup>Η NMR (CDCl<sub>3</sub>/TFA-d), δ: 8.25-7.90 (ArH-, m, backbone), 7.65 (ArH, s, cyclic dimer), 4.75-4.45 (COO-CH<sub>2</sub>-, m, backbone), 3.97 (HO-CH<sub>2</sub>-R, t-broad, end group), 3.82 (-CH<sub>2</sub>-O-CH<sub>2</sub>-, t, backbone DPG), 2.45-2.05 (-CH<sub>2</sub>-, m, backbone).

Copolymerization of Dimethylterephthalate, F<sub>10</sub>-iso, and 1,3-Propanediol. A 12.2 g sample of dimethylterephtalate, 30 g of the  $F_{10}$ iso prepared, and 17.25 g of 1,3-propanediol were charged to an ovendried 500 mL three necked round-bottom flask equipped with an overhead stirrer and a distillation condenser kept at 23 °C. The reactants were stirred under a nitrogen purge at a speed of 50 rpm. The contents were degassed three times by evacuating down to 100 Torr and refilling back to atmospheric pressure with N2 gas. TyzorTPT catalyst (13 mg) was added after the first evacuation. The reaction flask was immersed into a preheated metal bath set at 160 °C. The solids were allowed to completely melt at 160 °C for 20 min, after which the stirring speed was slowly increased to 180 rpm. The temperature was increased to 210 °C and maintained for 60 min. After 60 min, the nitrogen purge was discontinued, and a vacuum ramp was started such that after an additional 60 min the vacuum reached 50-60 mTorr. As the vacuum stabilized, the stirring speed was increased to 225 rpm and the reaction held for 3 h. The heat source was then removed. The overhead stirrer was stopped and elevated from the floor of the reaction vessel. The vacuum was then turned off and the system was purged with N2 gas at atmospheric pressure. The thus Scheme 1. General Route to Fluorinated Aromatic Ethers from Dimethyl 5-Hydroxyisophthalate



Figure 1. <sup>1</sup>H NMR (CDCl<sub>3</sub>) of fluorinated aromatic ethers from dimethyl 5-hydroxyisophthalate.

formed product was allowed to cool to ambient temperature. The product was recovered after carefully breaking the glass with a hammer. Yield = 90% of clear product. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.60 (ArH, s, 1H), 8.15–8.00 (ArH-, m, 2 + 4H), 7.65 (ArH, s, 4H), 6.15 (-CF<sub>2</sub>-CFH-O-, d, 1H), 4.70–4.50 (COO-CH<sub>2</sub>-, m, 4H), 3.95 (-CH<sub>2</sub>-OH, t, 2H), 3.85 (-CH<sub>2</sub>-O-CH<sub>2</sub>-, t, 4H), 2.45–2.30 (-CH<sub>2</sub>-, m, 2H), 2.10 (-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-, m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$ : 62.6, 62.4, 62.1, 62.0.

Copolymerization of Dimethylterephthalate, F<sub>16</sub>-iso, and 1,3-Propanediol. Dimethylterephthalate (30.1 g), F<sub>16</sub>-iso (100 g), and 1,3propanediol (42.6 g) were charged to an oven-dried 500 mL three necked round-bottom flask equipped with an overhead stirrer and a distillation condenser kept at 23 °C. The reactants were stirred under a nitrogen purge at a speed of 50 rpm. The contents were degassed three times by evacuating down to 100 Torr and refilling back to atmospheric pressure with N2 gas. TyzorTPT catalyst [40 mg] was added after the first evacuation. The flask was immersed into a preheated metal bath set at 160 °C. The solids were allowed to completely melt at 160 °C for 20 min after which the stirring speed was slowly increased to 180 rpm. The temperature was increased to 210 °C and maintained for 90 min. After 90 min at 210 °C, the nitrogen purge was discontinued, and a vacuum ramp was started such that after an additional 60 min the vacuum reached 50-60 mTorr. The reaction was held under stirring 180 rpm for 3 h still at 210 °C after which the reaction vessel was removed from the heat source. The overhead stirrer was stopped and elevated from the floor of the reaction vessel. The vacuum was then turned off and the system purged with N2 gas at atmospheric pressure. The thus formed product was allowed to cool to ambient temperature. The product was recovered after carefully breaking the glass with a hammer. Yield = 90% of a clear product. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.60 (ArH, s, 1H), 8.15-8.00 (ArH-, m, 2 + 4H), 7.65 (ArH, s, 4H), 6.15 (-CF<sub>2</sub>-

CFH-O-, d, 1H), 4.70–4.50 (COO-CH<sub>2</sub>-, m, 4H), 3.95 (-CH<sub>2</sub>-OH, t, 2H), 3.85 (-CH<sub>2</sub>-O-CH<sub>2</sub>-, t, 4H), 2.45–2.30 (-CH<sub>2</sub>-, m, 2H), 2.10 (-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-, t, 4H),  $^{13}$ C NMR (CDCl<sub>3</sub>),  $\delta$ : 62.6, 62.4, 62.1, 62.0.

Preparation of Blockcopolymers from 3-GF<sub>10</sub>-iso and PTT. A 20 g sample of PTT, and 46 g of 3-GF<sub>10</sub>-iso were charged to an oven-dried 250 mL three necked round-bottom flask equipped with an overhead stirrer and a distillation condenser kept at 23 °C. The reaction mass was kept under N2 purge atmosphere. The contents were degassed once by evacuating the reaction flask down to 150 mTorr and refilling back to atmospheric pressure with N<sub>2</sub> gas. TyzorTPT catalyst (20 mg) was added after the evacuation and repressurization. The nitrogen purge was then discontinued, and a vacuum ramp was started such that after about 30 min the vacuum reached a value of about 60 mTorr. The reaction flask was then immersed into a preheated metal bath set at 250 °C and the contents of the reaction flask were allowed to melt and equilibrate for 10 min. Stirring was initiated and speed was slowly increased to 180 rpm. The thus formed melt was left under vacuum with stirring for 15 min. The heat source was then removed. The overhead stirrer was then stopped and elevated from the floor of the reaction vessel. The vacuum was turned off, and the system was purged with N2 gas. The thus formed product was allowed to cool to ambient temperature. The product was recovered after carefully breaking the glass with a hammer. Yield: 91.2% of turbid product. <sup>13</sup>C NMR (tce $d_2$ ),  $\delta$ : 62.9 (E), 62.7 (D), 62.4 (G), 62.2 (F).

Preparation of Block Copolymers from 3-GF<sub>16</sub>-iso and PTT. A 15.3 g sample of PTT, and 46 g of 3-GF<sub>16</sub>-iso were charged to an oven-dried 250 mL three necked round-bottom flask equipped with an overhead stirrer and a distillation condenser kept at 23 °C. The reaction mass was kept under nitrogen purge. The contents were degassed once by evacuating down to 150 mTorr and refilling back to atmospheric pressure with N<sub>2</sub> gas. TyzorTPT catalyst (18 mg) was

added after the evacuation and repressurization. The nitrogen purge was then discontinued, and a vacuum ramp was started such that after about 30 min the vacuum reached a value of about 60 mTorr. The flask was then immersed into a preheated metal bath set at 250 °C, and the contents of the flask were allowed to melt and equilibrate for 10 min. Stirring was initiated and the speed was slowly increased to 180 rpm, and the molten contents of the flask was left under stirring for 60 min in the 250 °C bath. The heat source was then removed. The overhead stirrer was stopped and elevated from the floor of the reaction vessel. The vacuum was then turned off, and the system purged with N<sub>2</sub> gas. The thus formed product was allowed to cool to ambient temperature. The product was recovered after carefully breaking the glass with a hammer. Yield = 95.7% of an opaque product. <sup>13</sup>C NMR (tce- $d_2$ ),  $\delta$ : 62.9 (E), 62.7 (D), 62.4 (G), 62.2 (F).

#### DISCUSSION

Fluorinated Aromatic Ethers. Commercially available fluorinated monomers for step growth polymerization have



Figure 2. Structure and abbreviation of two fluorinated monomers,  $F_{10}$ -iso (i) and  $F_{16}$ -iso (ii).

traditionally been limited to tetrafluoroterephthalic acid. We have recently demonstrated the synthesis of fluorinated aromatic ethers via the addition of hydroxyl aromatic diesters to fluorinated vinyl ethers according to Scheme 1. Similar reactions with phenols were previously reported by Feiring.<sup>16</sup> We found that base-catalyzed conditions (enough to activate the hydroxyl aromatic diester) could be employed to drive the reaction. A range of strong bases was initially employed, including potassium tert butoxide, but it was found that milder bases, for example, sodium carbonate, could be used equally effective and with high practical importance. In a typical reaction the base, fluorinated vinyl ether, and the hydroxyl aromatic diester are combined in a polar solvent like THF, brought to reflux and left under stirring until complete

conversion is reached (typically within 16 h). Upon cooling, the base is filtered off, the solvent evaporated, and the product purified by distillation and obtained in high purity and yield.

Mechanistically, the hydroxyl aromatic diester, upon deprotonation, acts as nucleophile attacking the fluorinated double bond. Subsequent protonation of the carbanion completes the addition. Halogenated solvents, like carbon tetrachloride, or carbon tetrabromide may be employed, allowing formation of a functional halide, i.e., chloride or bromide, over the protonated product.<sup>4,17</sup> In this paper, we will only discuss the protonated form of the monomer. The product is fully supported by NMR. The <sup>1</sup>H NMR spectra is provided in Figure 1, for <sup>19</sup>F NMR see Supporting Information Figures SI 1 and SI 2. A characteristic tag for the NMR characterization is the H–F resonance that appears at ~6.25 ppm with a  $J_{\rm H–F}$ coupling constant of ~54 Hz.<sup>18</sup>

The described chemistry is suitable for a variety of fluorinated vinyl ethers and hydroxyl aromatic diesters. For example, both dimethyl 2-hydroxyterephthalate and dimethyl 5-hydroxyisophthalate are suitable nucleophiles, and 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2-trifluorovinyloxy) propane (PPVE) and 1,1,1,2,2,3,3-heptafluoro-3-(1,1,1,2,3,3-hexafluoro-3-(1,2,2-trifluorovinyloxy)propane (PPVE) were both employed electrophiles. In general, dimethyl 5-hydroxyisoph-thalate is preferred, since it provides a symmetric monomer for subsequent polymerizations.

The structures and abbreviations ( $F_{10}$ -iso and  $F_{16}$ -iso) of two highlighted monomers are depicted in Figure 2. The integers 10 and 16 simply refer to the number of fluorine atoms, and the iso refers to the dimethylester configuration on the aromatic ring. Although the dimethylester form of the monomer was used in subsequent polymerizations the fluorine side chain is robust toward several chemical transformations. For example, treatment of the diester in water/potassium hydroxide readily hydrolyzes the diester to the diacid and the monomer may be isolated after protonation. The diacid may be reacted with oxalyl or thionyl chloride to make the corresponding diacid chloride. Both these functional groups are suitable for either polyamide or polyaramid formation, importantly with retained fluorine functionalities.<sup>4</sup>

**Fluorinated Aromatic Homo- and Random Copolyesters.** The fluorinated monomers described above are suitable for a range of polycondensation protocols. We have been particularly interested in the use of these in polytrimethylene terephthalate (PTT) to impart oil repellency. PTT is the polymer of terephthalic acid (TPA) or dimethylterephthalate







Figure 3. <sup>1</sup>H NMR (CDCl<sub>3</sub>) of a polymeric fluorinated aromatic ether.

Table 1. Thermal Characteristics of  $3\text{-}GF_{10}\text{-}iso$  and  $3\text{-}GF_{16}\text{-}iso$  Homo- and Copolyesters

comonomer	mol % comonomer feed	mol % comonomer obtained <sup>a</sup>	$\overset{T_g}{(^\circ C)^b}$	${}^{T_{\mathfrak{m}}}_{(^{\circ}\mathcal{C})^{b}}$
PTT control	n/a	n/a	55	229
F <sub>16</sub> -iso	50	50	23	n/a
F <sub>10</sub> -iso	50	50	34	n/a
3-GF <sub>16</sub> -iso	100	100	5	n/a
3-GF <sub>10</sub> -iso	100	100	23	n/a
<sup>a</sup> From <sup>1</sup> H NMR (ratio of terephthalate to isophthalate). <sup>b</sup> From I				

 $(10^{\circ}/\text{min}, 2\text{nd heating scan}).$ 

(DMT) with 1,3-propanediol (PDO).<sup>19</sup> DuPont currently manufactures bio 1,3-propanediol (bio-PDO) from a fermentation process using corn based glucose as feedstock. The total biocontent in PTT is ~37 wt %. Standard polymerization protocols (diacid or diester routes) are depicted in Scheme 2 and the diester route will be explained in more detail.<sup>20</sup>

In the diester route an ester interchange reaction is initially conducted in which the dimethylester is exchanged for the glycol, typically employed in ~2-fold excess relative DMT. For PTT this means formation of a bishydroxypropyl intermediate of the corresponding aromatic diester. A typical ester interchange reaction temperature is ~200 °C in the presence of suitable transesterification catalyst, for example titanium(IV) isopropoxide. The ester interchange leads to condensation of methanol and can be easily monitored. Following ester interchange, which is completed within 1-2 h, the reaction temperature is increased and vacuum applied. Transesterification liberates the excess glycol and an increase in molecular weight is achieved after glycol distillation. A high molecular weight polymer is typically formed following 3-4 h at adequate vacuum and continuous agitation. The build of molecular weight may be monitored by a measurable increase in melt viscosity. Fluorinated homo and copolyesters were made by this



Figure 4. DSC comparison of PTT (top) and a fluorinated PTT copolymer containing 50 mol %  $F_{16}$ -iso (below).

method in which DMT partially, or fully, was replaced with  $F_{10}$ iso or  $F_{16}$ -iso and polymerized with bio-PDO resulting in 3-GF<sub>10</sub>-iso or 3-GF<sub>16</sub>-iso homo- or/and copolymers. Initial characterization of the fluorinated polymers were made from a combination of NMR techniques and size exclusion chromatography (SEC). <sup>1</sup>H NMR and <sup>19</sup>F-NMR confirmed the molecular structure, a general <sup>1</sup>H NMR of a polymeric fluorinated aromatic ether is depicted in Figure 3 (for <sup>19</sup>F NMR see Supporting Information Figures SI 3 and SI 4). From Figure 3, the resonance at ~6.15 ppm ( $J_{H-F} \sim 54$  Hz) is

#### **Macromolecules**



**Figure 5.** Comparison between copolymers and blends and the impact on fluorine efficiency.



Figure 6. DSC thermogram of PTT and 3-GF  $_{16}\mbox{-}iso$  (50 mol %) copolymer blend at 87.5/12.5 wt %.

indicative of an intact fluorine side chain. Additional backbone and end-group structures were similar to that of the PTT control, i.e., hydroxyl, methyl, and dipropylene glycol ends. Moreover, the polymer fluorine content corresponded with the monomer feed ratio. SEC traces are monomodal with  $M_w/M_n$  ratios ~2.0 indicative of a successful polycondensation (Supporting Information, Figure SI 5).

Thermal analysis has shown that the thermal characteristic of PTT is preserved if the fluorinated comonomer concentration is low (<3 mol %). However, increasing feed ratios of fluorinated monomer lead to depression of the PTT melting point, above a critical concentration of comonomers (>25 mol %) no crystallization is achieved indicating the formation of an amorphous copolymer. Table 1 summarizes the thermal characteristics of copolymers with similar levels of comonomer, and Figure 4 shows a typical DSC trace of PTT compared with a fluorinated copolymer containing 50 mol %  $F_{16}$ -iso.

Surface Properties of Fluorinated Aromatic Homoand Copolyesters. The surface properties of fluorinated homo- and copolymers were investigated using hexadecane as probe liquid. PTT completely wets hexadecane (i.e., contact angle  $<10^{\circ}$  or close to  $0^{\circ}$ ) whereas the 3-GF<sub>10</sub>-iso and 3-GF<sub>16</sub>iso homopolymers repel hexadecane. The highest contact angles measured were obtained after coating the homopolymers onto a PTT film substrate. The homopolymer was dissolved in



**Figure 7.** IPC chromatograms of calibration series (top, integer relates mol % F<sub>16</sub>-iso in copolymer), corresponding elution curve (middle), and chemical composition calibration curve (below).



**Figure 8.** IPC chromatograms of extruder derived melt blends (50/50 wt %) of PTT with a fluorinated copolymer ( $50 \text{ mol } \% 3\text{-}GF_{16}\text{-}iso$ , FNMB-91). Curves represent IPC chromatograms from dynamic extruder sampling at residence times 1–90 min.

Scheme 3. "Monomer First" (Top) vs "Oligomer First" (Bottom) Approach for 3-GF<sub>16</sub>-iso Based Copolymers



Figure 9. Visual difference between random (FNMB-43) and blocky copolyester (FNMB-105), copolymer composition is the same, i.e. 50 mol % PTT and 50 mol % 3-GF<sub>16</sub>-iso.

chloroform, the substrate coated, dried, and the resulting coating was analyzed for its hexadecane repellency. The average 3-GF<sub>10</sub>-iso and 3-GF<sub>16</sub>-iso hexadecane contact angles were  $\sim 63^{\circ}$  and  $\sim 76^{\circ}$  respectively.

Various routes were considered for a built-in fluorine approach. The first route involved copolymers in which a minor portion of DMT was replaced with the fluorinated monomer. The second route utilized blends in which a



Figure 10. SEC overlay of oligomers and chain extended copolymer.

fluorinated homopolymer was made and subsequently melt blended with neat PTT. When comparing these two routes, the blend approach showed an enhancement in hexadecane repellency compared with the copolymer approach. This can be illustrated by comparing the use of 1 wt % of  $F_{16}$ -iso (1 wt % total addition,  $\sim$  4640 ppm fluorine) utilized either in a copolymer or in a blend (99 wt % PTT + 1 wt % 3-GF<sub>16</sub>-iso). The net amount of fluorine is the same. However, blends provide an improvement of  $\sim 30^{\circ}$  when measuring advancing hexadecane contact angles, as depicted in Figure 5. An initial clue to the improved repellency was obtained during a design of experiment (DOE) study performed to elucidate the important parameters influencing repellency during the melt compounding process. The DOE was performed on a DSM microcompounder in which the additive concentration (1 and 5 wt %), fluorine monomer ( $F_{10}$ -iso and  $F_{16}$ -iso), mixing speed (extruder rpm 150 and 245), mixing time (extruder residence time 5 and 10 min), and temperature (kept constant at T = 260°C) were the in-going parameters. Interestingly, the main effects plot for hexadecane advancing contact angle showed that the extruder parameters (i.e., residence time and extruder speed) had a minor effect on repellency and that additive concentration and choice of monomer solely influenced repellency (Supporting Information, Figure SI 6). The result from the DOE suggests additive-matrix phase separation. Subsequent blend characterizations have been able to confirm this phenomenon and will be outlined in detail below.

Blend Characterization. Thermal DSC analysis is a robust method for checking compatibility of different polymer components. Miscible polymer blends follow the Fox equation and allow the prediction of a single blend glass transition temperature  $(T_g)$  from the overall blend composition and the  $T_{\sigma}$  of the individual polymer components.<sup>21</sup> The presence of two individual  $T_g$ 's for a two component blend is evidence of immiscibility and phase separation between the two components. For our study, blends were made with a sufficiently high loading of the fluorinated copolymer to have adequate resolution for the DSC analysis. PTT copolymers based on F<sub>16</sub>-iso (50 mol %) were blended with neat PTT (DSM conditions: T = 260 °C,  $t_{\text{mixing}} = 10$  minutes, extruder rpm=150) to provide final concentrations of 12.5, 25, and 50 wt % of the copolymer. Shown in Figure 6 below is the DSC thermogram of the blended material at 12.5 wt % incorporation (25 and 50 wt % identical but with more distinct transitions, see Supporting Information Figures SI 7 and SI 8). The two  $T_{\sigma}$ 's are distinct at ~23 °C and ~55 °C, indicative of phase separation between the fluorinated additive and PTT.

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#### Table 2. Molecular Weight Information of Oligomers and Chain Extended Copolymers

sample name	$M_{\rm n} \ ({\rm g/mol})^a$	$M_{\rm w}  ({ m g/mol})^a$	PDI <sup>a</sup>
1. 3-GF <sub>16</sub> -iso (FNMB-102)	9100	16600	1.82
2. PTT (FNMB-99)	8500	16100	1.89
3. Copolymer (FNMB-105, from FNMB-99 and FNMB-102)	59000	118500	2.01
<sup>a</sup> From SEC.			

Rf-IPA



Figure 11. DSC thermogram (1st heat) and structure of the blocky polyester,  $T_g(1)$  is from the fluorine component and  $T_g(2)$  and  $T_m$  from the PTT component.

#### Table 3. Thermal Characterization Summary

sample	$T_{g}$ (°C)	$T_{\rm m}$ (°C)	
3-GT	55	230	
3-GF <sub>16</sub> -iso	8	-	
copolymer, <sup>a</sup> random	23	-	
copolymer, <sup>a</sup> blocky	18, 54	219	
<sup>a</sup> Composition, 50 mol % 3-GT, 50 mol % 3-GF <sub>16</sub> -iso.			



Figure 12. UV (290 nm) IPC traces of random and blocky copolymers.



Figure 13. Different structural units in the fluorinated copolymer.



Figure 14. Available dyads in the fluorinated copolycondensate.

TPA



**Figure 15.** Different distributions of aliphatic carbon signal in random (top) vs blocky (below) copolymer composition.

SEC in combination with interaction polymer chromatography (IPC) was also used to characterize the blended materials. SEC provides molecular weight distributions by separating macromolecules by size, IPC complements SEC as it separates macromolecules based on functionality, independent of size. Typically, SEC is performed with a negligible enthalpic contribution, i.e., the column material (stationary phase) is made neutral to the polymer present in the eluent (mobile phase) so that only steric (entropic) interactions between the macromolecule and the stationary phase occur. In IPC, however, column materials are used which allow for a specific stationary phase-macromolecule attractive (adsorption) interaction, which depends on the chemical structure of the polymer. In IPC, steric and adsorption interactions compete with each other and at the so-called critical point of adsorption (CPA), elution independent of molecular weight is achieved.

Table 4. Degree	of Randomness	/Blockyness (B)	for Various	Copolymers

sample name	mol % 3-GF <sub>16</sub> -iso	$M_{\rm n}$ hard segment (g/mol)	$M_{\rm n}$ soft segment (g/mol)	condensation time (min)	B-value
FNMB-43 (random, control)	50	-	_	180	~1
FNMB-105	50	8500	9100	180	0.8
FNMB-109	50	8500	9100	90	0.63
FNMB-126	50	25800 <sup>a</sup>	9100	90	0.56
FNMB-132	50 <sup>b</sup>	8500	17100	30	0.56
approx 1 + 1 + 1 + 0 + 1 + but + 1	<b>.</b> .				

<sup>a</sup>PTT bright 1.02 I.V. <sup>b</sup>Using F<sub>10</sub>-iso as monomer.



Figure 16. Advancing hexadecane contact angles comparing a random melt additive with a blocky, both components containing 50 mol %  $F_{16}$ -iso.



Figure 17. Receding hexadecane contact angles comparing a random melt additive with a blocky, both components containing 50 mol %  $F_{16}$ -iso.

The CPA depends on the polymer chemical structure and not on the molecular weight, and continuous change of the mobile phase composition (gradient elution) provides the tool of separation.<sup>22</sup> To evaluate the effect of chemical composition on IPC retention, several statistical (random) copolymers of bio-PDO, DMT and  $F_{16}$ -iso at various mol % compositions, i.e., 10 mol %, 25 mol %, 50 mol %, 90 mol %, and 100%  $F_{16}$ -iso, were synthesized. These copolymers as measured by SEC (in hexafluoroisopropanol), have monomodal molecular weight distributions and PDI's ~2.0 (Supporting Information, Figure SI 9). IPC was conducted on the same series using a hydrophobic silica-gel bonded Si(CH2)2C8F17 stationary phase. The mobile phase was switched from neat HFIP to a gradient of water and HFIP (running from 60 vol % HFIP to neat HFIP). Shown in Figure 7 is an overlay of the IPC chromatograms from the UV absorbance detector (top), the chemical composition elution curve (middle), and the resulting IPC calibration curve (below). Notice that PTT does not exhibit any retention at these conditions and elutes with the initial solvent band (ca. 2 min retention time).

IPC was now performed on PTT/3-GF<sub>16</sub>-iso (50 mol %) melt blends, Figure 8. Only two components are present, the additive (retention time  $\sim 25$  min) and PTT (retention time  $\sim 2$ min). These retention times well match the expected values from the calibration curve, indicative of low levels of transesterification. Remarkably, the retention profile remained similar at long extruder residence times (1-90 min). From the dynamic extruder sampling study a minor peak shift following 90 min was observed suggesting a minor level of transesterification had occurred. One control experiment was additionally made and this time the melt generated blend was overlaid with the solution mixture of the same components (50/50 wt %). As expected these two materials display the exact same IPC chromatogram as the one viewed in Figure 8. Additional support for the observed increased hexadecane repellency has come from surface tension analysis. Using the mean harmonic method<sup>26</sup> (water and methyl iodide as probe liquids) surface tensions between 12 and 26 dyn/cm have been measured utilizing 1-5 wt % of either the  $3-GF_{10}$ -iso (50 mol %) or the 3-GF<sub>16</sub>-iso (50 mol %) additive in blends with PTT. As control, the surface tension of PTT was measured at ~41dyn/cm. Seemingly the reduced surface tension provided by the fluorinated additives creates a driving force for both surface migration and phase separation. The overall blend characterization suggests that PTT can be blended with fluorinated additives with limited intermolecular interactions occurring in the melt. Lack of transesterification explains the observed increase in hexadecane contact angle, since the low surface tension and higher additive mobility, relative to PTT, facilitates easier migration of fluorine to the material-air interface.

Development of Fluorinated Aromatic Blocky Copolyesters. One opportunity arising from the lack of melt induced transesterification is to control the microstructure of the fluorinated additive. The hypothesis was that by utilizing prepolymers/oligomers instead of monomers, with retained lack of transesterification during the condensation stage, the fluorinated additive form a blocky copolymer structure. To test this hypothesis, we performed a direct comparison between a "monomer first" approach with that of an "oligomer first" approach utilizing oligomers of PTT and the fluorinated homopolymer 3-GF<sub>16</sub>-iso. In both routes the overall composition was maintained the same, i.e. 50 mol % 3-GT and 50 mol % 3-GF  $_{\rm 16}\text{-iso.}$  A schematic depicted below (Scheme 3) shows the difference between these two approaches. Practically, the "monomer first" approach utilized standard polycondensation techniques as outlined above. However, in the "oligomer first" approach, the two starting materials were

made individually, subsequently combined, and copolymerized in the presence of a transesterification catalyst. The interesting result is that the "oligomer first" approach rendered an opaque material that appeared elastic. The difference in appearance is viewed in Figure 9.

Characterization verified chain extension of the two oligomers. Figure 10 shows an overlay of the molecular weight distributions (MWD) of the two starting oligomers (PTT and 3-GF<sub>16</sub>-iso) and the copolymer, as measured by SEC. The interesting observation is that no oligomer remains and that only one molecular weight distribution (of higher molecular weight) is obtained. Moreover, the copolymer is monomodal and the PDI is ~2.0 (Table 2). The expected PDI for a high molecular weight product of a regular polycondensation process is 2.0. Thus, chain extension of oligomers does not alter the behavior of a traditional polycondensation process, i.e., "monomer first" type. The two starting oligomers possessed  $M_n$  values close to 9 000 g/mol whereas the measured copolymer  $M_n$  was ~60 000 g/mol (Table 2). This indicates that the copolymer is a multiblock of the two starting materials.

Further support for chain extension came from hydroxyl endgroup characterization using <sup>1</sup>H NMR (tce-d2). Here the hydroxyl end-group concentration of the copolymer was compared with the oligomers. Typically hydroxyl end-group concentrations between 2 and 5 mol % were found in the oligomers whereas for the copolymer levels below 0.6 mol % was measured. These estimates was made by comparing the <sup>1</sup>H NMR signal of the hydroxyl group ( $\sim$ 3.80–3.85 ppm) with the combined signals of the fluorinated aromatic ether ( $\sim$ 8.6 ppm), terephthalate ( $\sim$ 8.0 ppm), and diester (4.35–4.65 ppm) group. It is to point out that the SEC characterization technique is preferred, over <sup>1</sup>H NMR, for high molecular weight polymers due to the relatively low end-group concentration in these systems.

Additional characterization of the chain extended copolymer was obtained by thermal DSC analysis (Figure 11). Results indicate that the thermal characteristics of the two starting components are retained in the copolymer, i.e. the  $T_{\sigma}$  from the fluorinated component is observed at ~18 °C and  $\breve{T}_{\rm g}$  and  $T_{\rm m}$ from the PTT component are observed at 54 and 219 °C, respectively. The  $T_g$  of the fluorinated component (~18 °C) is about 10 °C higher compared to the homo 3-GF<sub>16</sub>-iso oligomer  $(T_g \sim 8 \ ^{\circ}C)$ . The increase in  $T_g$  is ascribed to the fact that the chain ends now are incorporated into the copolymer and that this restriction in mobility leads to a slightly higher onset in translational mobility. Similarly, the  $T_{\rm m}$  of the PTT component is  $\sim 10$  °C lower compared to the neat polymer, due to the incorporation of the softer fluorinated component. As already described, the fully amorphous or random/statistical copolymer only shows a single  $T_{\rm g}$  ~ 23 °C (Table 1). Thus, overall findings suggest a blocky type of copolymer. In fact, the thermal characteristics are typical of thermoplastic elastomers (TPE's), which may explain the observed elastic properties of the resulting material. In Table 3 are summarized the thermal characteristics of the homo- and copolymers, either random or blocky.

We also analyzed the copolymer microstructure. We compared the chain extended copolymer with the random copolymer using IPC. As outlined above, IPC separates polymers based on their microstructure and we have recently shown that blockiness increases IPC retention, i.e. multiblock copolymers always elute later than the corresponding statistical counterpart with the same chemical composition.<sup>22</sup> As can be

seen in Figure 12 this trend is confirmed and the blocky copolymer elutes noticeably later than the statistical copolymer of the same chemical composition, i.e. 50 mol %  $F_{16}$ -iso.

We used <sup>13</sup>C NMR spectroscopy to determine sequence distributions in these polymers, and thus determine degree of randomness/blockiness. NMR is a well established method for studying polymer microstructures. For example sequence determination using <sup>1</sup>H NMR has been used to study stereo sequences in polylactides,<sup>23</sup> and <sup>13</sup>C NMR spectroscopy has been used to study the sequence distribution in copolyester/carbonate systems.<sup>24</sup> Quantitative <sup>13</sup>C NMR was used to determine the exact composition.

The blockiness index, B, is defined by Devaux,<sup>25</sup> op. cit., as

$$B = \frac{F_{12}}{2\sum_{i=1}^{2}F_{i}}$$

wherein  $F_{12}$  represents the total mole fraction of diads of first and second repeat units, in either sequence.  $F_i$  represents the mole fraction of structural repeat units (Figure 13).  $F_{12}$ ,  $F_{21}$ ,  $F_{11}$ , and  $F_{22}$  are the molar fractions of dyad repeat units in our copolymer structure, Figure 14. The blockiness index B is 0 for a diblock copolymer and 1 for a random copolymer.

The designation "G'' represents the NMR peak of the two OCH<sub>2</sub> carbons when two trimethylene terephthalate moieties are adjacent to one another; this dyad is designated TT; its mole fraction is  $F_{11}$ . The designation "D" represents the NMR peak of the two OCH<sub>2</sub> carbons when two 3-GF<sub>16</sub>-iso (or two 3- $GF_{10}$ -iso) moieties are adjacent to one another; this dyad is denoted FF; its mole fraction  $F_{22}$ . The designation "E" and "F" represent the two NMR peaks of the two different OCH<sub>2</sub> groups in the dyad which contains both a 3-GF<sub>16</sub>-iso (or 3- $GF_{10}$ -iso) moiety and a trimethylene terephthalate moiety. There are two statistically possible arrangements of this dyad, which are equivalent by NMR, designated FT and TF, with mole fractions  $F_{12}$  and  $F_{21}$ . The relative amount of the TT dyad is determined by the area of peak G/2, of the FF dyad by the area of D/2, and of the sum FT and TF dyads by the area of (E + F)/2. These dyad amounts can be normalized to 100% to give the mole fraction of each type of dyad. Each of the dyad mole fractions is thus determined as follows:

$$F_i = \frac{\int X_i}{\sum_{j=1-4} \int X_j}$$

In a random copolymer the statistical ratio of the dyad is 1:2:1 for TT:TF + FT:FF. In this case the areas of peaks D, E, F, G will be 1:1:1:1. Interestingly, the distribution of the aliphatic carbon signals G, D, E, and F are different depending on the composition of the copolymer as viewed in Figure 15. For a random copolymer the four signals, as expected, are equal in intensity whereas for a blocky copolymer signals D and G are enhanced relative to signals E and F. This information, in conjunction with the molar composition, can now be used to determine the degree of randomness/blockiness.

To demonstrate the ability to tune the copolymer blockiness the obtained B-values for a few selective copolymer compositions are summarized in Table 4. One interesting observation is that the overall condensation time impacts the final B-value. In the initial reaction (FNMB-105) the condensation time was kept deliberately long (180 min), yet the copolymer retains a blocky structure. By lowering the condensation time (FNMB 109) it appears as if the degree of blockiness increases, i.e., lower B-value. Another route to an increased blockiness is to utilize a higher molecular weight PTT hard segment. Sample FNMB-126 utilized a commercial grade PTT (bright, 1.02 IV) as starting material with a higher molecular weight. Blocky copolycondensates were also achieved utilizing the  $F_{10}$ -iso monomer, FNMB-132 in Table 4. Importantly the B-value for the random copolymer control (FNMB-43) was ~1. Likely other factors may influence the B-value, i.e. soft segment length and hard/soft segment ratio. Further aspects however will not be covered since the primary focus, of this paper, has been to demonstrate the initial proof of principle.

Repellency of Blocky Copolyesters. The blocky polyester (FNMB-105,  $M_{\rm p} \sim 59000$  g/mol) was melt blended with neat PTT bright ( $M_n \sim 25800 \text{ g/mol}$ , I.V. 1.02 mL/g) and evaluated for its hexadecane repellency. A comparison was made with a melt blend from an amorphous melt additive (FNMB-43,  $M_{\rm n} \sim 72900$  g/mol) of identical molar composition, i.e., 50 mol % PTT and 50 mol % 3-GF<sub>16</sub>-iso. The melt blends were prepared in a DSM micro compounder outlined above and extruded into ribbons (1 in. wide). The blocky melt additive seems to outperform the random additive when comparing advancing hexadecane contact angles, Figure 16. Moreover, receding hexadecane contact angles (Figure 17) are consistently higher for the blocky additive. In general, advancing contact angles represent the materials low surface energy component, whereas, the receding contact angle represents the materials high surface energy component.<sup>26</sup> A smaller contact angle hysteresis (difference between advancing and receding) is correlated with an improved surface homogeneity. Seemingly, our data suggests that the blocky additive provides a more homogeneous fluorinated surface as compared with the random additive.

In summary, melt-derived polycondensation was utilized to prepare block copolymers of two seemingly immiscible polymers. The forward condensation reaction is active although transesterification during normal melt blending is limited. Blockiness was found to be retained even at 180 min in the melt, under vacuum, and in the presence of a transesterification catalyst.<sup>27</sup> Melt additives based on blocky copolymers were shown to be more fluorine efficient compared to random copolymers and demonstrate an improvement in hexadecane repellency; in addition, they reduce the contact angle hysteresis.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Various analytical results including <sup>19</sup>F NMR data, SEC data, DSC data, and main effect plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Hougham, G.; Cassidy, P. E.; Johns, K.; Davidson, T. *Fluoropolymers 2, Properties*; Kluwer Academic: Dordrecht, The Netherlands, ISBN: 0-306-46061-0

(2) Drysdale, E. N.; Mahajan, S.; Moloy, K. G.; Nederberg, F.; Pollino, J.; Ritter, J. C. Fluoroether functionalized aromatic diesters and derivatives thereof, 2011, WO2011028767.

(3) Bunn, C. W.; Howells, E. R. Nature 1954, 549.

(4) Drysdale, E. N.; Mahajan, S.; Moloy, K. G.; Nederberg, F.; Pollino, J.; Ritter, J. C. Synthesis of polyesters comprising fluorovinylether functionalized aromatic moities for use as soil resistant fibers, 2011, WO2011028778.

(5) Drysdale, E. N.; Mahajan, S.; Moloy, K. G.; Nederberg, F.; Pollino, J.; Ritter, J. C. *Polyester films with improved oil repellency*, 2011, WO2011028771

(6) Drysdale, E. N.; Moloy, K. G.; Nederberg, F.; Pollino, J.; Ritter, J. C. Aramid comprising fluorovinylether functionalized moities, 2011, WO2011028791

(7) Carothers, W. H. J. Am. Chem. Soc. 1929, 51, 2548.

(8) Carothers, W. H. Chem. Rev. 1931, 8, 353.

(9) Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.

(10) (a) Yu, J.; Li, B.; Lee, S.; Ree, M. J. Appl. Polym. Sci. 1999, 73, 1191. (b) Li, B.; Yu., J.; Lee, S.; Ree, M. Polymer 1999, 40, 5371.
(c) Ubach, J.; Ilarduya, A. M.; Quintana, R.; Alla, A.; Rude, E.; Munoz-Guerra, S. J. Appl. Polym. Sci. 2010, 115, 1823.

(11) (a) Shyr, T.-W.; Lo, C.-M.; Ye, S.-R. Polymer 2005, 5284.
(b) Wei, G.; Wang, L.; Chen, G.; Gu, L. J. Appl. Polym. Sci. 2006, 100, 1511.
(c) Zou, H.; Li, G.; Jianming, J.; Shenglin, Y. Polym. Eng. Sci. 2008, 48 (3), 511.
(d) Castellano, M.; Marsano, E.; Turturro, A.; Canetti, M. J. Appl. Polym. Sci. 2011, 122 (1), 698.

(12) http://www2.dupont.com/Plastics/en\_US/Products/Hytrel/ Hytrel.html

(13) Tonelli, C.; Trombetta, T.; Scicchitano, M.; Simeone, G.; Ajroldi, G. J. Appl. Polym. Sci. **1996**, 59, 311.

(14) Iwashita, K.-I.; Yokoyama, A.; Yokozawa, T. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 4109.

- (15) Yokozawa, T.; Yokoyama, A. Prog. Polym. Sci. 2007, 147.
- (16) Feiring, A. A.; Wonchoba, E. R. J. Org. Chem. 1992, 57, 7014.
- (17) Koch, H. F.; Kielbania, A. J. J. Am. Chem. Soc. 1970, 92 (3), 729.
- (18) Ihrig, A. M.; Smith, S. L. J. Am. Chem. Soc. 1972, 94 (1), 34.
- (19) Bhatia, S. K.; Kurian, J. Biotechnol. Lett. 2008, 30, 619.

(20) Scheirs, J.; Long, T. E. Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters; Wiley: New York, ISBN 9780471498568, 2003.

(21) (a) Fox, T. G. Bull. Am. Phys. Soc. **1956**, 1, 123. (b) Gedde, U. Polymer physics; Kluwer Academic Publishers: Dordrecht, The Netherlands, ISBN 0-412-62649-3, 1999.

(22) (a) Brun, Y. J. Liq. Chrom. Rel. Technol. 1999, 22 (20), 3027.
(b) Brun, Y. J. Liq.Chrom. Rel. Technol. 1999, 22 (20), 3067. (c) Brun, Y.; Alden, P. J. Chrom. A 2002, 966, 25. (d) Chang, T. J. Polym. Sci., Part B: Polym. Phys. 2005, 43, 1591. (e) Brun, Y.; Foster, P. J. Sep. Sci. 2010, 33, 3501.

(23) (a) Kricheldorf, H. R.; Boettcher, C.; Tonnes, K.-U. *Polymer*1992, 33, 2817. (b) Kasperczyk, J. E. *Macromolecules* 1995, 28, 3937.
(c) Zhang, L.; Nederberg, F.; Messman, J. M.; Pratt, R. C.; Hedrick, J. L.; Wadem, C. G. J. Am. Chem. Soc. 2007, 129, 12610.

(24) (a) Pego, A. P.; Zhong, Z.; Dijkstra, P. J.; Grijpma, D. W.; Feijen, J. *Biomacromolecules* **2003**, 204, 747. (b) Kricheldorf, H. R.; Stricker, A. *Macromol. Chem. Phys.* **1999**, 200, 1726. (c) Kricheldorf, H. R. *Macromol. Chem. Phys.* **1979**, 2133.

(25) Devaux, J.; Godard, P.; Mercier, J. P. J. Pol. Sci. Pol. Phys. 1982, 20, 1875.

(26) Wu, S. Polymer Interface and Adhesion; ISBN 0-8247-1533-0; 1982.

(27) Note: General concept transferred into blocky copolyesters based on PET and PBT.