Block copolymers based on poly(vinylidene fluoride)
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The preparation of poly(3-hexylthiophene)-block-poly(vinylidene fluoride)-block-poly(3-hexylthiophene) (P3HT-b-PVDF-b-P3HT) is achieved through Grignard metathesis polymerization of 3-hexylthiophene and benzoyl peroxide initiated polymerization of vinylidene fluoride, followed by copper(I)-catalyzed azide-alkyne cycloaddition of the tailored P3HT and PVDF. A microphase separated melt was observed and confined crystallization of P3HT and PVDF occurred within the phase separated domains. The crystalline-crystalline triblock copolymers demonstrated rich phase behavior, leading to structural hierarchy at multiple length scales: from block copolymer microphase separation and semicrystalline P3HT lamellae, to lamellar packing of hexyl side chains and π-π stacking of polythiophene backbones.
3.1 Introduction

Driven by their ability to self-assemble into a wide range of morphologies on the nanoscale, block copolymers have been employed as building blocks for the fabrication of well-ordered nanomaterials. Microphase separation of AB-type diblock copolymers typically leads to spherical, cylindrical, gyroid or lamellar nanostructures, depending on the volume fractions of both block segments.\cite{1-6} More complex chain architectures give rise to the formation of even more fascinating morphologies. For instance, a vast variety of superlattice structures has been predicted by theory and discovered experimentally in linear ABC triblock copolymers due to the introduction of a third component.\cite{7-10} Remarkable Archimedean tiling patterns were reported in case of star-shaped ABC terpolymers having a single junction point.\cite{11-12}

The combination of self-assembly at different length scales leads to structure-in-structure formation.\cite{13-15} So-called hierarchical structures with double periodicity have been observed for the first time in supramolecules consisting of poly(styrene-block-4-vinylpyridine) (PS-b-P4VP) diblock copolymers and short pentadecyl phenol (PDP) side chains hydrogen-bonded to the pyridine blocks.\cite{16-17} This resulted in the formation of lamellar-in-lamellar and cylindrical-in-lamellar morphologies.\cite{17} An alternative approach to introduce hierarchy on the nanoscale involves binary multiblock copolymers with two-length-scale molecular architectures.\cite{12,14} Contrary to the previous system, just two chemically different species are sufficient to obtain hierarchically ordered structures. Experimental examples concern S-[I-S-I-S-I-S-I-S-I]-S undecablock copolymers\cite{18} composed of polystyrene (S) and polyisoprene (I) and S-[HS-S-HS-S-HS-S]-HS octablock copolymers\cite{19} composed of polystyrene and poly(\textit{para}-hydroxy styrene) (HS). In both cases, the linear multiblock copolymers consist of two large end blocks and multiple short middle blocks, and their self-assembly resulted in lamellar-in-lamellar morphologies with parallel double periodicity. The introduction of crystallizable segments in block copolymers may strongly influence the structure due to the competition between microphase separation and crystallization.\cite{20-21} Depending on the glass transition temperature ($T_g$), crystallization temperature ($T_c$), order-disorder transition temperature ($T_{ODT}$) and segregation strength, many different morphologies can be obtained.
Structural hierarchy in P3HT-\textit{b}-PVDF-\textit{b}-P3HT copolymers

Crystallization can be confined within the block copolymer microdomains in case of strongly segregated melts, while crystallization can dominate the structure formation for weakly segregated or homogeneous melt systems through breakout. Crystalline-amorphous block copolymers composed of both amorphous and crystallizable blocks received most attention.\cite{20-22} In block copolymers with all-crystallizable segments, \textit{i.e.} double-crystalline block copolymers, the competition in crystallization between the different components may also affect the structure formation.\cite{23} PLLA-\textit{b}-PVDF-\textit{b}-PLLA, described in Chapter 2, is an example of a double-crystalline block copolymer. In this chapter, the preparation and hierarchical structure formation of double-crystalline poly(3-hexylthiophene)-\textit{block}-poly(vinylidene fluoride)-\textit{block}-poly(3-hexylthiophene) (P3HT-\textit{b}-PVDF-\textit{b}-P3HT) will be discussed.

Poly(vinylidene fluoride) (PVDF) is an exceptional member of the fluoropolymer family, due to the piezo-, pyro- and ferroelectric character of the \(\beta\)-crystalline phase that arises from the strong dipole along the polymeric chain.\cite{24-25} Combined with its high thermal stability and chemical inertness, PVDF offers great potential for application in actuators, electronics and energy harvesting devices.\cite{26} Copolymerization of vinylidene fluoride with other fluoromonomers resulted in various commercial products, ranging from thermoplastics and elastomers to thermoplastic elastomers.\cite{27} Apart from these fluorinated random copolymers, well-architectured block copolymers containing PVDF segments have attracted attention.\cite{27}

PVDF-based block copolymers can self-assemble into well-ordered nanostructured materials with excellent properties as described above. Even though controlled radical polymerization methods commonly employed in block copolymer synthesis cannot be applied easily to the polymerization of fluorinated olefins,\cite{28} several well-defined PVDF-containing block copolymers have been prepared via alternative methods. For instance, chlorine-terminated PVDF, prepared via a radical polymerization of VDF initiated by chloromethyl benzoyl peroxide, has been employed to initiate the atom transfer radical polymerization (ATRP) of styrene.\cite{29} A similar macroinitiator has also been used to synthesize a macro-chain transfer agent suitable for reversible addition-fragmentation transfer (RAFT) polymerization, leading to PVDF-containing triblock copolymers with ionic liquid segments.\cite{30} In addition, techniques as iodine transfer polymerization (ITP)\cite{31-32}
and macromolecular design via the interchange of xanthates (MADIX)\textsuperscript{[33-35]} were performed to prepare other PVDF-based block copolymers. Recently, a click reaction involving the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) of azide-functionalized PVDF and alkyne-functionalized PS was performed to obtain PVDF-\textit{b}-PS copolymers.\textsuperscript{[36]} Nowadays, several synthetic strategies towards block copolymers with PVDF segments have been developed, however their crystallization and self-assembled structures received only little attention.

The popularity of conjugated poly(3-hexylthiophene) (P3HT) can be ascribed to its thermal and environmental stability, good processability and excellent electronic properties.\textsuperscript{[37-38]} Therefore, this semiconducting polymer offers great potential for organic (opto)electronic devices, such as field-effect transistors and organic photovoltaics.\textsuperscript{[38]} For instance, one of the most successful polymer-based solar cell systems in terms of efficiency contains blends of P3HT and phenyl-C61-butyric acid methyl ester (PCBM).\textsuperscript{[39]} To a lesser extent, the magnetic behavior in P3HT has also been investigated. Room temperature ferromagnetism was reported for P3HT partially doped with perchlorate (to introduce unpaired spins)\textsuperscript{[40-41]} and P3HT blended with PCBM.\textsuperscript{[42]} In addition, ferromagnetic behavior was demonstrated in several substituted poly(thiophene)s in their neutral state at 5K.\textsuperscript{[43-44]} Both semiconducting\textsuperscript{[45]} and magnetic\textsuperscript{[44]} properties are dependent on the extent of regioregularity in the polythiophene backbone. The large scale synthesis of regioregular P3HT, in which the polymer microstructure contains almost exclusively head-to-tail couplings, at room temperature became available by the development of Grignard metathesis (GRIM) polymerization by McCullough’s group in 1999.\textsuperscript{[46-47]} In GRIM polymerization, 2,5-dibromo-3-hexylthiophene reacts with an alkyl Grignard reagent to generate a mixture of regioisomers, and subsequent introduction of a catalytic amount of Ni(dppp)\textsubscript{2} affords poly(3-hexylthiophene) with typically 98\% head-to-tail couplings due to catalyst selectivity.\textsuperscript{[47]} This cross-coupling polymerization proceeds through a quasi-living chain growth mechanism, leading to well-defined molecular weights and narrow polydispersities.\textsuperscript{[48]} Besides regioregularity of the chains, the supramolecular organization and morphology can affect the properties of poly(3-alkylthiophene)s as well.\textsuperscript{[41,44,49]} Hence, the crystallization of P3HT has been the subject of several investigations.\textsuperscript{[49-53]} X-ray diffraction demonstrated that the crystalline poly(3-
hexylthiophene) structure involves two-dimensional sheets of \( \pi \)-stacked P3HT backbones separated by alkyl side chain layers.\(^{50-51}\) Brinkmann and co-workers uncovered an additional degree of order, namely the periodic alternation of crystalline lamellae separated by amorphous interlamellar zones, representing the semicrystalline superstructure of P3HT.\(^{52}\) In samples with higher molecular weight P3HT, they observed interconnection of the crystalline lamellae, and this enhanced connectivity may account for the increase in charge carrier mobility.\(^{54}\)

The ‘living’ character of the GRIM polymerization allows the preparation of end-functionalized P3HT. For instance, alkyne-terminated P3HT was successfully prepared by the addition of ethynylmagnesium bromide to the Ni-terminated P3HT synthesized by GRIM.\(^{55}\) The facile in situ end-group functionalization triggered the development of various P3HT-based block copolymers with improved or modified properties with respect to P3HT homopolymers.\(^{37-38}\) Several groups used vinyl- and allyl-terminated P3HT as precursor to synthesize P3HT-containing diblock copolymers via ATRP, RAFT, nitroxide-mediated polymerization (NMP) and even anionic polymerization.\(^{56-58}\) Another convenient approach involving click chemistry was introduced by Urien and co-workers, who synthesized a series of di- and triblock copolymers from ethynyl-terminated P3HT and azide-capped PS using azide-alkyne cycloaddition.\(^{59}\) This approach was adopted to obtain a broad range of P3HT-based rod-coil block copolymers,\(^{60-62}\) which can find potential application in field-effect transistors and organic solar cells.

In general, the self-assembly of block copolymers having P3HT segments is dictated by the crystallization of P3HT. The reported block copolymers often reveal a nanofibrillar morphology similar to regioregular P3HT homopolymers.\(^{57,63-64}\) Many studies consider the block copolymer phase separation in thin films,\(^{38}\) while investigations considering equilibrium structures in the bulk are scarce. Nevertheless, conventional spherical, cylindrical and lamellar morphologies have been detected in bulk samples of poly(3-hexylthiophene)-block-poly(2-vinylpyridine) for P3HT weight fractions below 50\%.\(^{58}\)

A few reports discuss the phase behavior of double-crystalline block copolymers, composed of P3HT and a secondary crystallizable component. Crystalline-crystalline block copolymers consisting of polyethylene (PE) and P3HT were developed in order to obtain tough semiconducting materials for flexible organic
electronics.\textsuperscript{[65]} Crystallization from both solution\textsuperscript{[66]} and melt phase\textsuperscript{[67]} has been studied, and rich phase behavior was observed. Solidification of P3HT prior to the insulating PE was demonstrated to be beneficial for inducing good electronic and mechanical properties.\textsuperscript{[66]} The competition between microphase separation and crystallization was investigated for all-conjugated double-crystalline poly(phenylene)-\textit{block}-poly(thiophene) diblock copolymers.\textsuperscript{[68]} By altering the block composition and the annealing process, the authors were able to tune this competition, thereby observing both confined and breakout crystallization phenomena. Another example of confined crystallization was reported for high molecular weight crystalline-liquid crystalline block copolymers.\textsuperscript{[69]} The high molar mass of both P3HT and poly(perylene bisimide acrylate) (PPerAcr) blocks ensured a high $\chi_N$ value and consequently microphase separation in the melt. Upon cooling, confined crystallization occurred inside the phase separated domains without destroying the microphase order, and typical lamellar and cylindrical morphologies were realized consistent with the respective volume fractions.

\begin{equation}
\text{Scheme 3.1 Synthesis route towards azide-terminated PVDF, alkyne-terminated P3HT and P3HT-\textit{b}-PVDF-\textit{b}-P3HT triblock copolymer.}
\end{equation}
This chapter reports the synthesis and self-assembly of a novel ABA block copolymer: poly(3-hexylthiophene)-block-poly(vinylidene fluoride)-block-poly(3-hexylthiophene) (P3HT-b-PVDF-b-P3HT). Copper(I)-catalyzed azide-alkyne coupling of PVDF with P3HT telechelics is carried out to obtain well-defined triblock copolymers (Scheme 3.1). Moreover, the self-assembly into hierarchical structures has been studied. Considering the reported properties of PVDF and P3HT, P3HT-b-PVDF-b-P3HT is a potential multiferroic material consisting of both fully organic ferroelectric and ferromagnetic segments. The resulting well-ordered nanostructured materials may find application in data storage devices and magnetic field sensors.\textsuperscript{[70-72]}

3.2 Experimental

3.2.1 Materials

Oxalyl chloride (Acros, 98%), α-bromo-\textit{p}-toluic acid (Acros, 97%), lithium peroxide (Li\textsubscript{2}O\textsubscript{2}, Acros, 95%), vinylidene fluoride (VDF, Synquest Labs, 98%), sodium azide (NaN\textsubscript{3}, Aldrich, 99.5+%), 2,5-dibromo-3-hexylthiophene (Aldrich, 97%), isopropylmagnesium chloride (\textit{i}-PrMgCl, Acros, 2.0M in THF), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni(dppp)Cl\textsubscript{2}, Aldrich), ethynylmagnesium bromide (Aldrich, 0.5 M in THF), copper(I) bromide (CuBr, Aldrich, 98+) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, Acros, 99+) were used as received. All solvents used were of analytical grade.

3.2.2 Synthesis of azide-terminated PVDF (3)

\textit{Step 1.} Oxalyl chloride (2.2 mL, 25 mmol) and a few drops of anhydrous DMF were added to a stirred suspension of α-bromo-\textit{p}-toluic acid (5.0 g, 23 mmol) in 25 mL of anhydrous DCM at 0 °C. After reacting for 2 h at room temperature, the solvent was removed by rotary evaporation. The remaining yellow residue was immediately dissolved in 50 mL \textit{n}-hexane/Et\textsubscript{2}O (1:1). The resulting solution was slowly added via a droplet funnel to a rapidly stirred 25 mL aqueous solution of Li\textsubscript{2}O\textsubscript{2} (1.3 g, 30 mmol) at 0 °C. After reacting for 2 h at room temperature, the reaction mixture was diluted with 250 mL chloroform and washed twice with 200 mL H\textsubscript{2}O. The aqueous phase was extracted twice with 100 mL chloroform. The combined organic phases were dried over MgSO\textsubscript{4} and chloroform was subsequently removed by rotary evaporation. The remaining white solid was
recrystallized from chloroform, yielding white needle-shaped crystals of 4-(bromomethyl)benzoyl peroxide (1). \(^1\)H-NMR (400 MHz, DMSO-\(d_6\), \(\delta\)): 8.02 (d, 4H, –ArH), 7.70 (d, 4H, –ArH), 4.80 (s, 4H, –PhCH\(_2\)Br).

**Step 2.** A solution of (1) (1.0 g, 2.4 mmol) in 300 mL of anhydrous acetonitrile was added to a pressure reactor (Figure 2.1: Parr Instruments, model 4568). The vessel was closed and purged with N\(_2\) for 30 min to degas the mixture. Subsequently, the reactor was charged with an initial pressure of 20 bar VDF, heated to 90 °C and stirred at 500 rpm. After reacting for 30 min, the vessel was cooled down to room temperature and depressurized. The reaction mixture was cooled to 0 °C, and the precipitate was collected by filtration. The remaining solid was washed with acetonitrile and chloroform. Reprecipitation was carried out from DMF in MeOH/H\(_2\)O (1:1), and the collected white solid was dried in vacuo at 40 °C to yield bromine-terminated PVDF (2). \(^1\)H-NMR (400 MHz, THF-\(d_8\), \(\delta\)): 8.03 (d, –ArH), 7.55 (d, –ArH), 4.61 (s, –PhCH\(_2\)Br), 4.61 (m, –COOC\(_2\)H\(_2\)CF\(_2\)Br, head-to-tail), 2.84 (m, –CF\(_2\)CH\(_2\)–CF\(_2\)CH\(_2\)–, tail-to-tail).

**Step 3.** NaN\(_3\) (53 mg, 0.82 mmol) was added to a solution of (2) (\(M_{n,GPC} = 15.9\) kg·mol\(^{-1}\), 1.0 g, 0.063 mmol) in DMF. The reaction mixture was stirred at 60 °C overnight, and subsequently precipitated in H\(_2\)O and washed with H\(_2\)O and EtOH. The collected dark-yellow solid was dried in vacuo at 40 °C to yield azide-terminated PVDF (3). \(^1\)H-NMR (400 MHz, THF-\(d_8\), \(\delta\)): 8.08 (d, –ArH), 7.49 (d, –ArH), 4.61 (m, –COOC\(_2\)H\(_2\)CF\(_2\)Br), 4.49 (s, –PhCH\(_2\)N\(_3\)), 2.84 (m, –CF\(_2\)CH\(_2\)–CF\(_2\)CH\(_2\)–, head-to-tail), 2.30 (m, –CF\(_2\)CH\(_2\)–CH\(_2\)CF\(_2\)–, tail-to-tail).

### 3.2.3 Synthesis of alkyne-terminated P3HT (4)

A typical procedure for the Grignard metathesis polymerization of 3-hexylthiophene is as follows: 2,5-dibromo-3-hexylthiophene (0.33 ml, 1.53 mmol) and 12 ml of anhydrous THF were added using degassed syringes to a dried round-bottom flask, followed by the addition of \(i\)-PrMgCl (0.76 mL, 1.53 mmol) via a degassed syringe. The flask was heated for 2 h at 50 °C. After cooling to room temperature, the polymerization was initiated by adding Ni(dppp)Cl\(_2\) (34 mg, 0.062 mmol) to the yellow solution. Ethynylmagnesium bromide (0.40 ml, 0.20 mmol) was added via a degassed syringe to the red reaction mixture after 10 min, followed by 30 mL MeOH after an additional 5 min. The purple solid was isolated via filtration and washed thrice with MeOH. The remaining product was dissolved
in chloroform, filtrated, reprecipitated in MeOH and dried in vacuo at room temperature, yielding dark-purple alkyne-terminated P3HT (4) (Table 3.1). The product was stored at -18 °C. $^1$H-NMR (400 MHz, THF-$d_8$, $\delta$): 7.08 (s, –ThH), 4.07 (s, HCC≡C–), 2.85 (t, –ThCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.73 (m, –ThCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.46-1.37 (m, –ThCH$_2$CH$_2$C≡CH$_2$CH$_3$), 0.92 (t, –ThCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$).

P3HT without alkyne functionality was prepared via the same procedure using HCl, instead of ethynylmagnesium chloride, to quench the reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[cat] (mM)</th>
<th>[M] (mM)</th>
<th>$M_{n,\text{theor}}$ (kg·mol$^{-1}$)</th>
<th>$M_{n,\text{GPC}}$ (kg·mol$^{-1}$)</th>
<th>PDI$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT$^3$</td>
<td>5.8</td>
<td>118</td>
<td>3.4</td>
<td>3.2</td>
<td>1.22</td>
</tr>
<tr>
<td>P3HT$^4$</td>
<td>4.8</td>
<td>118</td>
<td>4.2</td>
<td>3.7</td>
<td>1.18</td>
</tr>
<tr>
<td>P3HT$^5$</td>
<td>3.8</td>
<td>118</td>
<td>5.2</td>
<td>4.6</td>
<td>1.12</td>
</tr>
</tbody>
</table>

$^a$ $T$ = 25 °C; $t$ = 10 min; [i-PrMgCl] = 118 mM; [ethynyl-MgBr] = 15 mM. $^b$ Determined from [M]/[cat] ratio. $^c$ Determined by GPC of precipitated product in THF.

### 3.2.4 Synthesis of P3HT-b-PVDF-b-P3HT (5)

A typical procedure for CuAAC of PVDF and P3HT is as follows: CuBr (14 mg, 0.10 mmol), (3) ($M_{n,\text{GPC}} = 15.9$ kg·mol$^{-1}$, 100 mg, 6.3 µmol) and (4) ($M_{n,\text{GPC}} = 3.7$ kg·mol$^{-1}$, 75 mg, 20 µmol) were added to a dried round-bottom flask, followed by a degassing procedure (i.e. evacuating and backfilling three times with N$_2$). 5.0 mL of anhydrous DMF was added via a degassed syringe, followed by PMDETA (0.031 mL, 0.15 mmol), and the reaction was stirred for 3 days at 70 °C. The mixture was precipitated in MeOH/H$_2$O (1:1) and washed with MeOH/H$_2$O (1:1) and MeOH. The remaining product was thoroughly rinsed with chloroform to remove unreacted P3HT homopolymers, yielding dark-purple P3HT-b-PVDF-b-P3HT (5) (Table 3.2). $^1$H-NMR (400 MHz, THF-$d_8$, $\delta$): 8.03 (d, –ArH), 7.45 (d, –ArH), 7.08 (s, –ThH), 5.73 (s, –PhCH$_2$Tr–), 4.61 (m, –COOC$_2$H$_5$), 2.84 (m, –CF$_2$CH$_2$CF$_2$–, head-to-tail), 2.84 (t, –ThCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 2.30 (m, –CF$_2$CH$_2$–CH$_2$CF$_2$–, tail-to-tail), 1.73 (m, –ThCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.46-1.37 (m, –ThCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 0.92 (t, –ThCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$).
Table 3.2 Conditions\(^a\) and characteristics of P3HT-b-PVDF-b-P3HT triblock copolymers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>P3HT (^1) polymer</th>
<th>[P3HT] (mM)</th>
<th>[PVDF] (mM)</th>
<th>(M_n) (kg·mol(^{-1}))</th>
<th>(f_{P3HT})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P3HT(^3)</td>
<td>4.0</td>
<td>1.6</td>
<td>22.3</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>P3HT(^4)</td>
<td>4.0</td>
<td>1.3</td>
<td>23.3</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>P3HT(^5)</td>
<td>4.0</td>
<td>1.6</td>
<td>25.1</td>
<td>0.37</td>
</tr>
</tbody>
</table>

\(^a\) [PMDETA] = 1.5·[CuBr] = 30 mM; \(T = 70 ^\circ\)C; \(t = 3\) days.

3.2.5 Preparation of block copolymer films

A 0.5% w/w solution of P3HT-b-PVDF-b-P3HT in THF was stirred for at least 2 h at 60 °C. The solution was filtered and subsequently poured into a glass Petri dish. The solvent was allowed to evaporate and the film was subsequently annealed in solvent vapor at room temperature for two weeks, yielding a dark-purple film with a thickness of \(\text{ca.}\ 20 \mu\text{m}\).

3.2.6 Characterization

Differential scanning calorimetry (DSC) was carried out using a TA Instruments Q1000 in N\(_2\) atmosphere. Samples of approximately 5 mg were encapsulated in aluminum pans, and during the measurement a heating/cooling rate of 10 °C/min was applied.

Polarized optical microscopy (POM) was conducted on a Zeiss Axiophot and samples were placed between crossed polarizers. Thin films were prepared between microscope cover slips by melting the polymer at 240 °C, and subsequently cooled in a Mettler FP82HT hot stage to room temperature prior to imaging. To enhance the contrast, a \(\lambda\) wave plate was inserted between the polarizers.

Wide-angle X-ray scattering (WAXS) and Small-angle X-ray scattering (SAXS) were performed at the Dutch-Belgium Beamline (DUBBLE) station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.\(^{[73-74]}\) The sample-detector distance of the SAXS set-up was \(\text{ca.}\ 5\) m, while the X-ray wavelength was 1.03 Å. The scattering vector \(q\) is defined as \(q = 4\pi/\lambda\sin\theta\) with \(2\theta\) being the scattering angle. Temperature-resolved measurements were performed using a Linkam DSC 600 cell.
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Additional SAXS experiments were performed at the University of Groningen using an advanced NanoStar setup, \textit{i.e.} an assembly of a NanoStar camera and a Microstar X-ray generator (both by Bruker AXS). The sample-detector distance was \textit{ca.} 24 cm. The parameters of the rotating anode X-ray generator were 45 kV and 60 mA, the flux of the primary X-ray beam at the sample position was estimated to be $8 \times 10^8$ photons⋅s$^{-1}$⋅mm$^{-2}$ and the size of the beam was about 0.4 mm in diameter. Temperature-resolved measurements were performed using an Anton Paar TCU50 temperature control unit.

Bright-field transmission electron microscopy (TEM) was carried out on a Philips CM12 transmission electron microscope operating at an accelerating voltage of 120 kV. Prior to embedding, pieces of the film were thermally annealed in the DSC using the following procedure: heating to 240 °C with 10 °C/min, annealing at 240 °C for 1 min, cooling to 20 °C with 10 °C/min. TEM samples were prepared as follows: ultrathin sections (\textit{ca.} 80 nm) of a block copolymer film embedded in epoxy resin (Epofix, Electron Microscopy Sciences) were microtomed using a Leica Ultracut UCT-ultramicrotome equipped with a 35° Diatome diamond knife at room temperature, and subsequently placed on copper grids. The samples were stained with I$_2$ for 30 min prior to imaging to enhance the contrast.

Gel permeation chromatography (GPC) was performed in stabilized THF or CHCl$_3$ (flow rate of 1 mL min$^{-1}$) on a Viscotek GPC equipped with three detectors (Viscotek Ralls detector, Viscotek Viscometer Model H502 and Shodex RI-71 Refractive Index detector), using a guard column (PLgel 5 µm Guard, 50 mm and two columns PLgel 5 µm MIXED-C, 300 mm, Agilent Technologies) at 30 °C. Molecular weights of PVDF homopolymers and block copolymers were calculated relative to PS according to universal calibration using narrow disperse standards (Agilent Technologies and Polymer Laboratories). Molecular weights of P3HT homopolymers were measured using triple detection.

$^1$H nuclear magnetic resonance ($^1$H-NMR) spectra were recorded on a 400 MHz Varian VXR operating at room temperature.

Fourier transform infrared (FTIR) spectroscopy measurements were performed using KBr pellets \textit{in vacuo} in transmission mode on a Bruker IFS 66v/S equipped with a DTGS detector at a resolution of 4 cm$^{-1}$. 

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Chapter 3

3.3 Results and discussion

3.3.1 Synthesis

Copper(I)-catalyzed azide-alkyne cycloaddition of end-functionalized P3HT and PVDF resulted in the successful synthesis of P3HT-b-PVDF-b-P3HT triblock copolymers. Bifunctional azide-terminated PVDF has been prepared via benzoyl peroxide initiated polymerization of vinylidene fluoride and additional end-group modification, while Grignard metathesis polymerization of 3-hexylthiophene led to alkyne-capped P3HT (Scheme 3.1).

Benzoyl peroxides tailored with a wide variety of functional groups have demonstrated to act as effective initiators for the synthesis of telechelic fluoropolymers, and the synthesis of well-defined bromine-terminated PVDF using 4-(bromomethyl)benzoyl peroxide as initiator has been discussed in detail in Chapter 2. Br-PVDF-Br (2) was reacted with sodium azide in order to introduce the desired azide moieties onto PVDF chain ends (Scheme 3.1). Figure 3.1a depicts the \(^1\)H-NMR spectrum of the resulting azide-capped PVDF (3), in which the peaks corresponding to N\(_3\)PVDF-N\(_3\) are marked with “V”. The signals have been assigned in more detail in the experimental section. The upfield shift of the \(^1\)H-NMR singlet from 4.61 to 4.49 ppm (Figure 3.2a,b) attributed to the methylene protons designated with “M”, indicates full conversion from bromine to azide functionality. Furthermore, FTIR analysis (Figure 3.3a,b) confirmed the azide formation, according to the N=N=N stretch vibration observed in the spectrum at 2111 cm\(^{-1}\).

In contrast to conventional free radical polymerization of hydrocarbon alkenes, in which termination often occurs via combination and disproportionation, leading to broad dispersities, the benzoyl peroxide initiated polymerization of fluoromonomers generally results in well-defined products due to the absence of disproportionation as termination mechanism. Hence, a polydispersity of 1.25 was determined for azide-terminated PVDF with a number average molecular weight (\(M_{n,GPC}\)) of 15.9 kg·mol\(^{-1}\) according to GPC (Figure 3.4). End-group analysis based on \(^1\)H-NMR (Figure 3.1a), comparing VDF backbone protons with terminal aromatic protons, revealed a number average molecular weight (\(M_{n,NMR}\)) of 18.4 kg·mol\(^{-1}\), in good agreement with GPC measurements.
Figure 3.1 $^1$H-NMR spectra in THF-$d_8$ of (a) azide-terminated PVDF (b) alkyne-terminated P3HT and (c) P3HT-$b$-PVDF-$b$-P3HT block copolymer. Signals corresponding to PVDF and P3HT are designated with “V” and “T” respectively, while “e” labels the signal corresponding to the ethynyl end-group of P3HT. Remaining peaks correspond to THF and H$_2$O.

Figure 3.2 $^1$H-NMR spectra in THF-$d_8$ of (a) bromine-terminated PVDF, (b) azide-terminated PVDF and (c) P3HT-$b$-PVDF-$b$-P3HT block copolymer. Signals corresponding to methylene protons are designated with “M”.
Figure 3.3 FTIR spectra of (a) bromine-terminated PVDF, (b) azide-terminated PVDF, (c) P3HT, (d) alkyne-terminated P3HT and (e) P3HT-b-PVDF-b-P3HT block copolymer.

Functionalized regioregular P3HT (4) has been prepared from dibromohexylthiophene and isopropylmagnesium chloride via Ni-catalyzed GRIM polymerization, similar to literature procedures. Ethynylmagnesium bromide was introduced to end-cap the active chain end and quench the polymerization, resulting in alkyne-functionalized P3HT (Scheme 3.1). To remove residual catalyst traces, the crude product was dissolved in chloroform, filtered and reprecipitated in methanol. In this manner, Soxhlet extraction at elevated temperatures inducing alkyne-alkyne homocoupling was circumvented. Since homocoupling was even observed in the polymer product when stored at room temperature (Figure 3.5), samples were stored at -18 °C directly after purification. A variety of P3HT-C≡CH homopolymers have been synthesized (Table 3.1) by altering the ratio between monomer (M) and catalyst (cat). The molar mass calculated from the GPC trace ($M_{n,GPC}$) (Figure 3.4) is in excellent agreement with the theoretical predicted molecular weight ($M_{n,\text{theor}}$) (Table 3.1) determined from the [M]/[cat] ratio. Moreover, the monomodal GPC curve confirms the absence of undesired homocoupling. Rather narrow polydispersities of 1.1-1.2 were obtained, characteristic for GRIM polymerizations.
Figure 3.4 GPC traces of alkyne-terminated P3HT (dotted), azide-terminated PVDF (dashed) and P3HT-b-PVDF-b-P3HT block copolymer (solid) in THF.

Figure 3.5 GPC traces in CHCl₃ of alkyne-terminated P3HT stored at room temperature (dotted) and stored at -18 °C (solid) for 7 days.
The characteristic $^1$H-NMR signals corresponding to the P3HT backbone are designated with “T” in Figure 3.1b, and have been assigned in the experimental section in more detail. The incorporation of the ethynyl (“e”) end-group was confirmed by the singlet at 4.07 ppm. In addition, the FTIR spectrum (Figure 3.3d) shows the characteristic band at 3309 cm$^{-1}$ attributed to the terminal alkyne moiety.$^{76}$ Pristine P3HT homopolymers without ethynyl functionality, prepared via the same procedure using HCl instead of ethynylmagnesium chloride to quench the GRIM polymerization, consequently lack the signal for C≡C–H stretch vibration (Figure 3.3c).

Click chemistry was carried out between alkyne-terminated P3HT and azide-terminated PVDF in order to obtain P3HT-$b$-PVDF-$b$-P3HT copolymers (5), as presented in Scheme 3.1. Signals corresponding to both coupling partners were observed in the $^1$H-NMR spectrum of the precipitated product (Figure 3.1c). Additional end-group analysis demonstrated a strong downfield shift of the $^1$H-NMR singlet from 4.49 to 5.73 ppm (Figure 3.2b,c) for the initial end-group protons of functionalized PVDF. Together with the disappearance of the singlet assigned to the terminal ethynyl moiety of P3HT (Figure 3.1b,c), this indicates full conversion of the CuAAC click reaction. To support these findings, FTIR analysis was carried out, and both azide (2111 cm$^{-1}$) and alkyne (3309 cm$^{-1}$) end-groups were vanished in the spectrum representing the block copolymer product (Figure 3.3e).

The azide-alkyne cycloaddition of PVDF with P3HT$^3$, P3HT$^4$ and P3HT$^5$ (superscript is $M_n$,$\text{GPC}$ in kg·mol$^{-1}$) resulted in the formation of three distinct triblock copolymers (Table 3.2). The number average molecular weight ($M_n$) and weight fraction of P3HT ($f_{P3HT}$) were calculated from the predetermined $M_n$,GPC of both telechelics. From the GPC trace of P3HT-$b$-PVDF-$b$-P3HT 2 (Table 3.2, entry 2) in Figure 3.4, a $M_n$,GPC of 22.1 kg·mol$^{-1}$ has been determined correlating well with the expected molecular weight of 23.3 kg·mol$^{-1}$. The monomodal distribution, representing a polydispersity of 1.32, confirms the absence of unreacted homopolymers.

3.3.2 Structure and crystallization

Structural analysis has been performed for all block copolymer samples. Below, P3HT-$b$-PVDF-$b$-P3HT 2 (Table 3.2, entry 2) will be discussed in detail. The results for the remaining two block copolymers (entry 1,3) are comparable unless otherwise noted.
The crystallization of the block copolymer and its respective homopolymers was studied by DSC. Figure 3.6b displays the crystallization curve corresponding to the block copolymer sample. P3HT is the higher temperature crystallizing entity, which is revealed by the exothermic shoulder (shown in the inset) with a crystallization onset of 156 °C, similar to the parent homopolymer (Figure 3.6a). The weak signal indicates that the molten PVDF chains hinder the P3HT crystallization. PVDF crystallizes at slightly lower temperatures, having a $T_c$ of 142 °C, similar to the crystallization temperature of pristine PVDF homopolymer, already discussed in Chapter 2 (Figure 2.8).

The microstructure of a PVDF/P3HT homopolymer blend reveals a macrophase separated system upon cooling from the melt, consisting of both PVDF and P3HT domains (Figure 3.7a). In agreement with DSC, P3HT crystallizes first around 155 °C, representing the dark phase. At a slightly lower temperature of ca. 140 °C, PVDF spherulites are formed inside the other domains. Contrary, the optical micrograph of P3HT-$b$-PVDF-$b$-P3HT demonstrates a single phase system (Figure 3.7b). In contrast to double-crystalline PLLA-$b$-PVDF-$b$-PLLA triblock copolymers (Chapter 2) and P3HT-$b$-PE diblock copolymers, a clear spherulitic microstructure is absent. When stronger thermodynamic segregation between
both blocks in double-crystalline diblock copolymers is present, spherulite formation is hindered and more distorted microstructures are observed.\textsuperscript{[23]} The absence of a spherulitic morphology therefore indicates a (strongly) segregated melt.

\textbf{Figure 3.7} POM images of (a) PVDF/P3HT\textsuperscript{A} blend after cooling from the melt and (b) P3HT-\textit{b}-PVDF-\textit{b}-P3HT block copolymer \textbf{2} after cooling from the melt. Both images were recorded at room temperature.
Structural hierarchy in P3HT-\textit{b}-PVDF-\textit{b}-P3HT copolymers

Figure 3.8 (a) SAXS pattern of P3HT-\textit{b}-PVDF-\textit{b}-P3HT 2 recorded at room temperature after cooling from the melt and (b) Bright-field TEM image of the lamellar-in-lamellar nanostructure in P3HT-\textit{b}-PVDF-\textit{b}-P3HT block copolymer 2 after cooling from the melt. The microtomed section was stained with I$_2$ prior to imaging to selectively stain the P3HT domains.

The SAXS intensity profile of P3HT-\textit{b}-PVDF-\textit{b}-P3HT (Figure 3.8a) collected after cooling from the melt indicates a lamellar nanostructure. The characteristic domain spacing is calculated from the value of the first-order reflection $q^*$ at 0.139 nm$^{-1}$ and satisfies 45 nm. The TEM image (Figure 3.8b) confirms the lamellar morphology in the block copolymer material, and the observed length scale is in good agreement with the calculated domain spacing. Moreover, the micrograph surprisingly reveals a structure-in-structure morphology.

The final morphology in crystalline-crystalline block copolymers depends on the competition between microphase separation and crystallization. To investigate the formation of the remarkable structure observed in Figure 3.8b, several temperature-resolved X-ray scattering experiments have been carried out. Detailed information about the crystalline structure of the individual blocks can be obtained from the scattering patterns in Figure 3.9. The appearance of the (100) reflection at $q = 3.8$ nm$^{-1}$ (1.6 nm) in the SAXS intensity profiles (Figure 3.9a) indicate the lamellar packing of alkyl side chains in P3HT.\textsuperscript{\[51-52\]} The crystallization temperature of 160 °C is in agreement with the thermal behavior observed in DSC (Figure 3.6b). In addition, the WAXS patterns (Figure 3.9b) reveal the (020) reflection at $q = 16.5$ nm$^{-1}$ (0.38 nm), appearing at the same temperature,
corresponding to the π-π interchain stacking of P3HT.\textsuperscript{51-52} PVDF crystallizes at 140 °C, indicated by the strong signals at 12.6, 13.1 and 14.1 nm\(^{-1}\) attributed to the (100), (020) and (110) crystal planes, respectively, of in the α-polymorph. The results confirm that separate (nano)domains of crystalline P3HT and PVDF are formed in the block copolymer material.

A phase separated melt was observed for all P3HT-\textit{b}-PVDF-\textit{b}-P3HT block copolymers in SAXS (Figure 3.10b), thus at \(T = 240 \, ^\circ\text{C}: T_c < T < T_{ODT}\). Similar segregated melt systems were obtained for other P3HT-based block copolymers,\textsuperscript{67,69} although higher molecular weights in the range of 13-20 kg·mol\(^{-1}\) were reported for the P3HT segments. Upon cooling below the crystallization temperature of both segments, the position of the main peaks remains constant (Figure 3.10a), indicating that crystallization of the components is not altering the microphase separated structure. Apparently, the block incompatibility is sufficiently high to prevent breakout of the structure due to crystallization, and confined crystallization of PVDF and P3HT segments occurs inside the phase separated domains without destroying the order. In other words, the phase separated nanostructure directs the crystallization of P3HT segments, and in turn, the PVDF blocks crystallize under the restriction of the pre-crystallized P3HT phase. The observed phase behavior is in strong contrast with PLLA-\textit{b}-PVDF-\textit{b}-PLLA triblock copolymers described in Chapter 2, in which phase separation was completely driven by crystallization from the homogenous melt (\(T_c > T_{ODT}\)).
Figure 3.10 SAXS patterns of P3HT-\textit{b}-PVDF-\textit{b}-P3HT block copolymer recorded (a) at room temperature after cooling from the melt and (b) in the melt at 240 °C.

Figure 3.11 presents the observed nanostructure in more detail, revealing the remarkable lamellar-in-lamellar morphology. The proposed hierarchical structure, a result of the rich phase behavior of P3HT-\textit{b}-PVDF-\textit{b}-P3HT triblock copolymers, is schematically presented in Figure 3.12. The large length scale of 45 nm represents the block copolymer phase separation of PVDF and P3HT segments, as observed in the SAXS intensity profile of Figure 3.8a. We propose that the smaller length scale of approximately 10 nm, visible in TEM, arises from the semicrystalline lamellar organization of P3HT (confined inside the phase separated domains) into crystalline lamellae, which appear dark in the bright-field TEM images, separated by amorphous interlamellar zones. This semicrystalline structure was already observed in P3HT homopolymers.\cite{52,54} In this particular case, since the semicrystalline P3HT lamellae are parallel to the block copolymer lamellae, only the overall large length scale periodicity can be observed in SAXS. The scattering patterns in Figure 3.9 already demonstrated that the crystalline structure of P3HT involves π-π stacked backbones (0.38 nm) separated by alkyl side chain layers (1.6 nm). The amorphous zones in between most probably contain chain ends, folds and structural defects. The PVDF segments crystallize into the α-phase, in which the chains exhibit the \textit{trans-gauche} conformation.
Figure 3.11 (a,b) Bright-field TEM images of the lamellar-in-lamellar nanostructure in P3HT-b-PVDF-b-P3HT block copolymer 2. The microtomed section was stained with I$_2$ prior to imaging to selectively stain the P3HT domains.

Figure 3.12 Schematic representation of the proposed hierarchical structure in P3HT-b-PVDF-b-P3HT block copolymers based on X-ray scattering and electron microscopy measurements. The light and dark gray layers present the contrast in the TEM micrographs (Figure 3.11), green and red are P3HT and PVDF chains respectively. The length scale corresponding to the semicrystalline P3HT lamellae is estimated (ca. 10 nm) from TEM, since it cannot be observed in SAXS.

3.4 Conclusion

The successful synthesis of well-defined poly(3-hexylthiophene)-block-poly(vinylidene fluoride)-block-poly(3-hexylthiophene) is achieved via copper(I)-catalyzed azide-alkyne coupling of azide-functionalized PVDF and ethynyl-
terminated P3HT, prepared via benzoyl peroxide initiated polymerization and Grignard metathesis polymerization, respectively. The double-crystalline block copolymers microphase separate in the melt. Upon cooling, confined crystallization of P3HT, followed by PVDF, occurs inside the segregated domains. The α-polymorph of PVDF is obtained after crystallization from the melt. In addition, both lamellar packing of the alkyl side chains and π-π interchain stacking are observed in crystalline P3HT.

The rich phase behavior of the P3HT-b-PVDF-b-P3HT triblock copolymers results in an elegant structure characterized by hierarchical order at multiple length scales: 1) π-π stacking between polythiophene backbones (0.38 nm), 2) lamellar packing of alkyl side chains (1.6 nm), 3) semicrystalline lamellar organization of P3HT (ca. 10 nm) and 4) block copolymer microphase separation of PVDF and P3HT (45 nm). This remarkable self-assembly can be highly useful for future device fabrication.

### 3.5 References

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