Block copolymers based on poly(vinylidene fluoride)
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Double-crystalline poly(L-lactide)-block-poly(vinylidene fluoride)-block-poly(L-lactide) (PLLA-b-PVDF-b-PLLA) triblock copolymers were successfully synthesized through ring opening polymerization of L-lactide and benzoyl peroxide initiated polymerization of vinylidene fluoride, followed by copper(I)-catalyzed azide-alkyne coupling of the PLLA and PVDF telechelics. The block copolymers were miscible in the melt, and an alternating crystalline lamellar nanostructure was formed upon crystallization from the homogeneous melt. Crystallization behavior of the PLLA component depends strongly on the block composition. The crystallization temperature of the lower temperature crystallizing PLLA block increased considerably with respect to its parent homopolymer for rather symmetric block copolymers, indicating a strong nucleation effect, while on the other hand asymmetric block copolymers with low PLLA content demonstrated a large depression of crystallization temperature, due to a fractionated crystallization process. A confined crystallization mechanism for the PLLA blocks was suggested, indicated by the low degree of crystallization compared to the respective homopolymers, and confirmed by microstructure analysis performed during isothermal crystallization. Contrary to PLLA, crystallization of the higher temperature crystallizing PVDF component within the block copolymer was not influenced by block composition and similar crystallization behavior was observed with respect to PVDF homopolymers.

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Chapter 2

2.1 Introduction

The introduction of crystallinity in block copolymers results in a complex interplay between microphase separation and crystallization, leading to the generation of fascinating morphologies. While in conventional amorphous block copolymers the self-assembly is triggered by the thermodynamic repulsion between its components provoking microphase segregation,\(^{[1-4]}\) the incorporation of crystallizable blocks generally complicates the morphological features due to the competition of crystallization with phase segregation. Depending on the segregation strength in the melt, crystallization will be confined within the block copolymer microdomains (for strongly segregated melts), or crystallization can overwrite any preformed structure (for weakly segregated or homogeneous melts).

The most commonly studied crystallizable block copolymers are crystalline-amorphous, in which one of the blocks is amorphous and the other semicrystalline.\(^{[5-8]}\) Three key transition temperatures play an important role in the final morphology, \(i.e.\) the crystallization temperature (\(T_c\)), the glass transition temperature (\(T_g\)) of the amorphous block and the order-disorder transition temperature (\(T_{ODT}\)). If \(T_{ODT} > T_g > T_c\), the crystallization of the crystallizable block takes place within the phase segregated domains connected to the glassy component (hard confinement), and the microphase separated structure of the melt, \(e.g.\) cylindrical, spherical or lamellar, is generally preserved.\(^{[9]}\) If \(T_{ODT} > T_c > T_g\), the second component is above its \(T_g\), \(i.e.\) rubbery, and crystallization therefore occurs with little morphological constraint (soft confinement), enabling a possible break-out from the ordered melt structure.\(^{[9]}\) In that case, crystallization will overwrite the preformed melt morphology, leading to an alternating crystalline-amorphous lamellar nanostructure regardless of the block composition. Finally, if \(T_{ODT} < T_c > T_g\), crystallization occurs from a homogeneous melt, and microphase separation is completely driven by crystallization, generally leading to a lamellar nanostructure, again regardless of composition, within a spherulitic microstructure.\(^{[10]}\)

In block copolymers containing only crystallizable components, the competition between crystallization of the different crystalline blocks plays a more important role than the effect of microphase separation. In such double-crystalline block
Sequential crystallization of PLLA-\textit{b}-PVDF-\textit{b}-PLLA copolymers, the crystallization of one block may affect the crystallization and morphology of the other. The crystallization and structure of several double-crystalline di- and triblock copolymers has been investigated and reviewed.\cite{6,11} So far, mainly biodegradable block copolymers, composed of semicrystalline poly(ethylene oxide) (PEO), poly(\varepsilon-caprolactone) (PCL), poly(lactic acid) (PLA) or poly(\textit{p}-dioxanone) (PPDX), have been the subject of publications. When the copolymers are quenched from the melt, different situations can be observed, depending on crystallization temperatures, molecular weights and segregation strength. For the latter, as for crystalline-amorphous diblock copolymers, strongly segregated, weakly segregated and homogeneous melt systems are reported.\cite{11} If the melting temperatures for both components of a double-crystalline block copolymer are similar, as for PEO-\textit{b}-PCL, coincident crystallization of both blocks from the melt can occur for symmetric block ratios.\cite{12} The \textit{T}_c values of the block copolymer components compared to their parent homopolymers can be either lower\cite{13} (depression) or higher\cite{14} (nucleation effect). Often a strong depression in \textit{T}_c of the lower temperature component, \textit{i.e.} the block that crystallizes second from the melt, is revealed when the fraction of that concerning component is low.\cite{12,14} This phenomenon, called fractionated crystallization, is a consequence of the confined crystallization of the lower temperature block within the matrix of the higher temperature block that has crystallized previously.\cite{6,11} On the other hand, if the melting temperatures of the two blocks of a double-crystalline block copolymer are far from each other, \textit{e.g.} in PLLA-\textit{b}-PEO and PLLA-\textit{b}-PCL, separate crystallization temperatures have been reported.\cite{15-16} Again, differences between the \textit{T}_c values of the block copolymer components compared to the corresponding homopolymers have been observed for this situation, as well as fractionated crystallization. In certain cases the degree of crystallization of the lower temperature block has been reported to be very low,\cite{17} confirming the influence of the previously crystallized higher temperature component.

In terms of morphology, double-crystalline block copolymers generally form an alternating crystalline lamellar nanostructure, since crystallization is often the dominating self-organizing mechanism.\cite{11} Consequently, spherulites are observed as superstructure at the microscale. Several distinct birefringence patterns were obtained depending on the components, block composition and isothermal
crystallization temperature, e.g. (double) concentric,\textsuperscript{[14,18-19]} ring-banded,\textsuperscript{[20]} regular non-banded,\textsuperscript{[16]} granular\textsuperscript{[21]} and deformed spherulites.\textsuperscript{[21]}

Considering PLLA-b-PCL, the spherulitic structure is formed during the crystallization of the higher temperature PLLA block, and the morphology remains invariable during the sequential crystallization of the lower temperature PCL component. Only the magnitude of the birefringence changed, as indicated by the difference of brightness and color in POM images.\textsuperscript{[16]} Apparently, the previously formed crystalline PLLA matrix strongly templates the crystallization of PCL in such a way that this block has to fit in between the radially grown PLLA lamellae without altering the preformed superstructure. Similar results were reported for PLLA-b-PEO block copolymers.\textsuperscript{[22]}

This chapter discusses the preparation and crystallization of poly(L-lactide)-\textit{block}-poly(vinylidene fluoride)-\textit{block}-poly(L-lactide) (PLLA-b-PVDF-b-PLLA), a double-crystalline triblock copolymer. The synthesis route towards this material involves ring opening polymerization (ROP) of L-lactide (LLA), benzoyl peroxide initiated polymerization of vinylidene fluoride (VDF), and subsequential “clicking” of the end-functionalized PLLA and PVDF using copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC), as pointed out in Scheme 2.1.

\textbf{Scheme 2.1} Synthesis route towards azide-terminated PVDF, alkyne-terminated PLLA and PLLA-b-PVDF-b-PLLA triblock copolymer.
Sequential crystallization of PLLA-\textit{b}-PVDF-\textit{b}-PLLA copolymers

Click chemistry encompasses a wide range of reactions characterized by efficiency, selectivity and tolerance to functional groups and a variety of solvents. Popular and most widely used is the copper(I)-catalyzed azide-alkyne cycloaddition, a very general, robust, insensitive and orthogonal reaction between an azide and alkyne to form a triazole moiety.\cite{23-24} During the last decade, CuAAC has been employed extensively for the ligation of polymer fragments into block- and graft copolymers or other well-defined macromolecules,\cite{25-27} including fluorinated copolymers.\cite{28}

Poly(vinylidene fluoride) (PVDF) demonstrates outstanding thermal, chemical and mechanical stability,\cite{29} and is therefore applied in the industrial fabrication of pipes, linings, and automotives. However, most appealing are the reported ferro-, pyro- and piezoelectric properties of its β-crystalline phase.\cite{30-31} Consequently, many techniques have been developed to increase this popular β-polymorph in PVDF and PVDF-based materials, including mechanical stretching of the non-polar α-phase,\cite{31} solution casting from polar solvents\cite{32} or the addition of nanoclays.\cite{33}

Ferroelectric β-phase PVDF may find application in actuators, sensors and energy harvesting devices.\cite{34-35}

The incorporation of PVDF segments in block copolymers is highly attractive, since PVDF-containing block copolymers can function as potential precursors for ordered nanostructured materials with outstanding properties as described above. However, controlled radical polymerization techniques, commonly used to synthesize well-architected block copolymers, are not applied easily to the polymerizations of fluorinated olefins like PVDF.\cite{36} Nevertheless, PVDF-based block copolymers with reasonable chain lengths and polydispersities have been prepared using macroinitiator approach. For example, chlorine-terminated PVDF has been employed to initiate the atom transfer radical polymerization (ATRP) of styrene (S)\cite{37-38} and methyl methacrylate (MMA).\cite{37} Furthermore, techniques as reversible addition-fragmentation transfer (RAFT) polymerization,\cite{39} macromolecular design via the interchange of xanthates (MADIX)\cite{40} and iodine transfer polymerization (ITP)\cite{41} were performed to obtain alternative fluorinated-based block copolymers. In addition, Vukićević and co-workers performed a click reaction involving the CuAAC of alkyne-terminated PS and azide-terminated PVDF, prepared from an iodine-terminated PVDF precursor,\cite{42} for the synthesis of PVDF-\textit{b}-PS.\cite{43} Despite these efforts, studies reporting the crystallization and morphology of PVDF-containing block copolymers are rare.
Due to the chiral nature of lactic acid and its cyclic dimer lactide, polymerization can yield semicrystalline poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) or amorphous poly(LD-lactide) (PLDLA). In recent years, PLLA gained clinical attention due to its biodegradable and biocompatible properties, and has been used predominately in biomedical applications, for example sutures, scaffolds and orthopedic fixation devices. Due to its facile degradability in mild aqueous base, this polymer has also been employed to create nanoporous templates from block copolymer precursors, using polylactide as sacrificial block. Other PLLA-based block copolymers, containing perfluoropolyether (PFPE) segments, demonstrated improved melt processability, stronger surface hydrophobicity, increased ductility and elongation, and controlled environmental stability over PLLA homopolymers. Interesting is the reported shear piezoelectricity of PLLA after uniaxial orientation, achieved by mechanical stretching, and observed ferroelectric hysteresis when PLLA is electrically poled. Uniaxially drawn PLLA rods implanted in fractured shinbone even demonstrated an enhancement in bone formation (and therefore fracture healing) with respect to undrawn PLLA, which is attributed to the piezoelectric current generated by the mechanical strain accompanying leg movement.

In the absence of epimerization, ring opening polymerization (ROP) of enantiomerically pure L-lactide will lead to isotactic poly(L-lactide) PLLA. Bulk ROP of ε-caprolactone (CL) using an acetylene-functionalized alcohol as initiator resulted in well-defined alkyne-terminated poly(ε-caprolactone) (PCL), and a similar strategy will be used in this study to prepare alkyne-terminated PLLA with narrow polydispersities.

In this chapter, we investigate the preparation, structure and crystallization of a new double-crystalline triblock copolymer: PLLA-b-PVDF-b-PLLA. Azide-alkyne coupling is performed to “click” tailored PVDF and PLLA, allowing the preparation of well-defined copolymers with different block ratios (Scheme 2.1). The mutual interaction between the two crystallizable blocks will be studied by investigating the morphology as function of temperature, thereby determining the dependence of block composition and the difference from the behavior of parent homopolymers and blends.
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers

2.2 Experimental

2.2.1 Materials
Oxalyl chloride (Acros, 98%), α-bromo-p-toluic acid (Acros, 97%), lithium peroxide (Li₂O₂, Acros, 95%), vinylidene fluoride (VDF, Synquest Labs, 98%), sodium azide (NaN₃, Aldrich, 99.5+%), (3S)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione (L-lactide, Acros, 98%), tin(II) 2-ethylhexanoate (Sn(Oct)₂, Aldrich, 95%), 5-hexyn-1-ol (Aldrich, 96%), 1-hexanol (Aldrich, 99+%), 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.

2.2.2 Synthesis of azide-terminated PVDF (3)
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-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 resulting yellow residue was immediately dissolved in 50 mL n-hexane/Et₂O (1:1). The resulting solution was slowly added via a droplet funnel to a rapidly stirred 25 mL aqueous solution of Li₂O₂ (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 H₂O. The aqueous phase was extracted twice with 100 mL chloroform. The combined organic phases were dried over MgSO₄ 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). ¹H-NMR (400 MHz, DMSO-d₆, δ): 8.02 (d, 4H, –ArH), 7.70 (d, 4H, –ArH), 4.80 (s, 4H, –PhCH₂Br).

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 N₂ 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/H₂O (1:1), and the collected white solid was dried *in vacuo* at 40 °C to yield bromine-terminated PVDF (2). ¹H-NMR (400 MHz, acetone-δ₆, δ): 8.11 (d, −ArH), 7.69 (d, −ArH), 4.76 (s, −PhCH₂Br), 4.73 (m, −COOCH₂CF₂−), 2.98 (m, −CF₂CH₂−CF₂CH₂−, head-to-tail), 2.39 (m, −CF₂CH₂−CH₂CF₂−, tail-to-tail). ¹⁹F-NMR (400 MHz, acetone-δ₆, δ): -92.4 (−CH₂CF₂−CH₂CF₂−CH₂CF₂−, head-to-tail), -96.2 (−CH₂CF₂−CF₂CH₂−CH₂CF₂−CH₂CF₂−), -114.7 (−CH₂CF₂−CH₂CF₂−CF₂CH₂−), -117.0 (−CH₂CF₂−CF₂CH₂−CH₂CF₂−).

**Step 3.** NaN₃ (53 mg, 0.82 mmol) was added to a solution of (2) (Mₙ,GPC = 18.3 kg·mol⁻¹, 1.0 g, 0.055 mmol) in DMF. The reaction mixture was stirred at 60 °C overnight, and subsequently precipitated in H₂O and washed with H₂O and EtOH. The collected dark-yellow solid was dried *in vacuo* at 40 °C to yield azide-terminated PVDF (3). ¹H-NMR (400 MHz, acetone-δ₆, δ): 8.19 (d, −ArH), 7.66 (d, −ArH), 4.76 (m, −COOCH₂CF₂−), 4.67 (s, −PhCH₂N₃), 2.98 (m, −CF₂CH₂−CF₂CH₂−, head-to-tail), 2.39 (m, −CF₂CH₂−CH₂CF₂−, tail-to-tail).

**Figure 2.1** (a) Picture and (b) schematic representation of high pressure reactor set-up.
2.2.3 Synthesis of alkyne-terminated PLLA (4)

A typical procedure for the ring opening polymerization of lactide is as follows: L-lactide (1.9 g, 13.1 mmol) was added to a dried round-bottom flask, followed by a degassing procedure (i.e. evacuating and backfilling three times with N₂). The flask was heated to 130 °C to melt the L-lactide. 1-hexyn-5-ol (0.073 ml, 0.67 mmol) and 2 drops of Sn(Oct)₂ were subsequently added via degassed syringes and the solution was stirred for 30 minutes. During the reaction the mixture became solid, indicating the successful polymerization of LLA. The product was dissolved in DCM, precipitated in Et₂O and washed with Et₂O and MeOH. Reprecipitation was carried out from DCM in MeOH and the resulting white solid was dried in vacuo at 40 °C to yield alkyne-terminated PLLA (4) (Table 2.1).³¹H-NMR (400 MHz, CDCl₃, δ): 5.16 (m, –OCOC(CH₃)–), 4.35 (q, –OCOC(H(CH₃)OH), 4.16 (q, CH≡CCH₂CH₂CH₂CH₂O–), 2.23 (dt, CH≡CCH₂CH₂CH₂CH₂CH₂O–), 1.96 (s, CH≡CCH₂CH₂CH₂CH₂O–), 1.77 (m, CH≡CCH₂CH₂CH₂CH₂O–), 1.57 (s, –OCOCH(CH₃)–), 1.41 (d, –OCOCH(CH₃)OH).

PLLA without alkyne functionality was prepared via the same procedure using 1-hexanol, instead of 1-hexyn-5-ol, as initiator. The resulting alkane-terminated PLLA was used in homopolymer and blend studies to compare its crystallization with block copolymer samples.

<table>
<thead>
<tr>
<th>Product</th>
<th>I (mmol)</th>
<th>M (mmol)</th>
<th>t (min)</th>
<th>Mₙ,thor a (kg·mol⁻¹)</th>
<th>Mₙ,GPC c (kg·mol⁻¹)</th>
<th>PDI c</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA³</td>
<td>0.67</td>
<td>13.1</td>
<td>30</td>
<td>2.8</td>
<td>3.4</td>
<td>1.05</td>
</tr>
<tr>
<td>PLLA⁹</td>
<td>0.67</td>
<td>39.3</td>
<td>60</td>
<td>8.5</td>
<td>8.7</td>
<td>1.08</td>
</tr>
<tr>
<td>PLLA¹²</td>
<td>0.67</td>
<td>52.4</td>
<td>60</td>
<td>11.2</td>
<td>12.4</td>
<td>1.13</td>
</tr>
</tbody>
</table>

a T = 130 °C; [SnOct₂] = 2 drops. b Determined from [M]/[I] ratio. c Determined by GPC of precipitated product in THF.

2.2.4 Synthesis of PLLA-b-PVDF-b-PLLA (5)

A typical procedure for CuAAC of PVDF and PLLA is as follows: CuBr (14 mg, 0.10 mmol), (3) (Mₙ,GPC = 18.3 kg·mol⁻¹, 183 mg, 0.010 mmol) and (4) (Mₙ,GPC = 3.4 kg·mol⁻¹, 68 mg, 0.020 mmol) were added to a dried round-bottom flask, followed by a degassing procedure (i.e. evacuating and backfilling three times with N₂). 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 60 °C. The mixture was precipitated in cold MeOH/H$_2$O (1:3) and washed with MeOH/H$_2$O (1:1) and MeOH. Finally, the collected yellow-brown product was dried in vacuo at 40 °C to yield PLLA-b-PVDF-b-PLLA (5) (Table 2.2). $^1$H-NMR (400 MHz, acetone-$d_6$), $\delta$: 8.12 (d, –ArH), 7.83 (s, –TrH), 7.50 (d, –ArH), 5.75 (s, –PhCH$_2$Tr–), 5.26 (m, –OCOCH(CH$_3$)–), 4.71 (m, –COOC$_2$H$_4$CF$_2$–), 4.36 (m, –OCOCH(CH$_3$)OH), 4.21 (m, –TrCH$_2$CH$_2$CH$_2$CH$_2$O–), 2.98 (m, –CF$_3$CH$_2$–CF$_2$CH$_2$–head-to-tail), 2.39 (m, –CF$_3$CH$_2$–CH$_2$CF$_2$–tail-to-tail), 1.77 (m, –TrCH$_2$CH$_2$CH$_2$CH$_2$O–), 1.61 (m, –OCOCH(CH$_3$)–), 1.44 (d, –OCOCH(CH$_3$)OH).

Table 2.2 Conditions and characteristics of PLLA-b-PVDF-b-PLLA triblock copolymers.

<table>
<thead>
<tr>
<th>Product</th>
<th>PVDF polymer</th>
<th>[PVDF] (mM)</th>
<th>PLLA polymer</th>
<th>[PLLA] (mM)</th>
<th>$M_n$ (kg·mol$^{-1}$)</th>
<th>$f_{PLLA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{14}V_{72}L_{14}^{25}$</td>
<td>PVDF$^{18}$</td>
<td>2.0</td>
<td>PLLA$^{3}$</td>
<td>4.0</td>
<td>25.1</td>
<td>0.27</td>
</tr>
<tr>
<td>$L_{24}V_{52}L_{24}^{36}$</td>
<td>PVDF$^{18}$</td>
<td>2.0</td>
<td>PLLA$^{9}$</td>
<td>4.0</td>
<td>35.7</td>
<td>0.49</td>
</tr>
<tr>
<td>$L_{29}V_{42}L_{29}^{43}$</td>
<td>PVDF$^{18}$</td>
<td>2.0</td>
<td>PLLA$^{12}$</td>
<td>4.0</td>
<td>43.1</td>
<td>0.58</td>
</tr>
</tbody>
</table>

$^a$ [PMDETA] = 1.5·[CuBr] = 30 mM; $T$ = 60 °C; $t$ = 3 days.

2.2.5 Preparation of block copolymer films
A 1.5% w/w solution of PLLA-b-PVDF-b-PLLA in DMF was stirred for at least 1 h at room temperature. The solution was filtered and subsequently poured into a glass Petri dish. The solvent was allowed to evaporate slowly at 45 °C for two days and the film was subsequently annealed in solvent vapor for at least one week, yielding a yellow-brown film with a thickness of ca. 50 µm.

2.2.6 Preparation of homopolymer blends
Bromine-terminated PVDF and alkane-terminated PLLA homopolymers were dissolved in DMF in a 1:2 molar ratio, equal to the equivalents used for the CuAAC. For DSC analysis, the solution was added dropwise into an aluminum pan. The solvent was allowed to evaporate at 80 °C and the blend was subsequently dried in vacuo at 40 °C for 1 h before measurement. For POM measurements, the polymer solution was added dropwise onto a microscope cover slip. The solvent was allowed to evaporate at 80 °C and the blend was subsequently dried in vacuo at 40 °C for 1 h before analysis.
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers

2.2.7 Characterization

Differential scanning calorimetry (DSC) was carried out using a TA Instruments Q1000 in N₂ 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 190 °C, and quickly cooled in a Mettler FP82HT hot stage to the isothermal crystallization temperature (125 or 145 °C) prior to imaging. To enhance the contrast, a λ wave plate was inserted between the polarizers.

Gel permeation chromatography (GPC) of PVDF homopolymers was performed in DMF (flow rate of 1 mL min⁻¹) with 0.01 M LiBr on a Viscotek GPCMAX equipped with model 302 TDA detectors, using two columns (PSS-Gram-1000/30, 10 μ 30 cm). Molecular weights were calculated relative to PMMA according to universal calibration using narrow disperse standards (Polymer Laboratories). GPC of PLLA homopolymers was performed in stabilized THF (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 were calculated relative to PS according to universal calibration using narrow disperse standards (Agilent Technologies and Polymer Laboratories).

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (Maldi-ToF MS) measurements were performed on a Biosystems Voyager-DE PRO spectrometer, in positive and linear mode, by accelerating the voltage to 20 kV. Dithranol was used as matrix, sodium trifluoroacetate as salt for cationization and THF as solvent.

¹H and ¹⁹F nuclear magnetic resonance (¹H-NMR and ¹⁹F-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 in vacuo in transmission mode on a Bruker IFS 66v/S equipped with a DTGS detector at a resolution of 4 cm⁻¹.
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.\textsuperscript{[54-55]} The sample-detector distance of the SAXS set-up was \textit{ca.} 3.5 m, while the X-ray wavelength was 1.03 Å. The scattering vector $q$ is defined as $q = \frac{4\pi}{\lambda} \sin \theta$ with $2\theta$ being the scattering angle. Temperature-resolved measurements were performed using a Linkam DSC 600 cell.

Bright-field transmission electron microscopy (TEM) was carried out on a Philips CM12 transmission electron microscope operating at an accelerating voltage of 120 kV. 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.

### 2.3 Results and discussion

#### 2.3.1 Synthesis

PLLA-$b$-PVDF-$b$-PLLA triblock copolymers were successfully synthesized via copper(I)-catalyzed azide-alkyne cycloaddition of PLLA and PVDF telechelics. Alkyne-terminated PLLA has been prepared by ring opening polymerization of L-lactide, while benzoyl peroxide initiated polymerization of vinylidene fluoride and additional end-group modification led to azide-terminated PVDF (Scheme 2.1).

![Figure 2.2](image-url) (a) $^{19}$F-NMR spectrum and (b) $^1$H-NMR spectrum of bromine-terminated PVDF\textsuperscript{18} in acetone-$d6$. Signals corresponding to PVDF backbone are designated with “V”.

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\[ \text{Figure 2.2} \]
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers

Figure 2.3 ¹H-NMR spectra in acetone-δ6 of (a) bromine-terminated PVDF¹⁸, (b) azide-terminated PVDF¹⁸ and (c) L₁₄V₇₂L₁₄²⁵ block copolymer. Signals corresponding to methylene and triazole protons are designated with “M” and “T” respectively.

Benzoyl peroxides tailored with a wide variety of functional groups have demonstrated to act as efficient initiators for the synthesis of end-capped poly(vinylidene fluoride) and other fluoropolymers.⁵⁶ For example, chlorine-terminated PVDF is prepared via benzoyl peroxide initiated polymerization and can subsequently be employed as macroinitiator to initiate ATRP of styrene (Chapter 4). Using a similar approach outlined in Scheme 2.1, we successfully synthesized bromine-functionalized benzoyl peroxide (1) via acylation of Li₂O₂ with 4-(bromomethyl)benzoyl chloride, followed by the preparation of bromine-terminated PVDF (2) using the functionalized benzoyl peroxide as initiator. Both ¹⁹F-NMR and ¹H-NMR (Figure 2.2) depict the characteristic signals (assigned in the experimental section) for head-to-tail and tail-to-tail VDF sequences in the polymer backbone, indicating the successful synthesis of Br-PVDF-Br. The absence of disproportionation in termination⁵⁷–⁵⁸ is supported by the absence of resonances due to unsaturated bonds in the ¹H-NMR spectrum. Hence, propagating radicals are only consumed through combination, leading to well-defined phenylmethyl bromine end-groups at 8.11, 7.69 and 4.76 ppm (Figure 2.3a), in agreement with previous studies.⁵⁸ Traces of −CH₂−CF₃H (6.33 ppm) and −CF₂−CH₃ (1.83 ppm) moieties can be attributed to chain transfer reactions, like intramolecular backbiting that results in short chain branches.⁵⁹
Chapter 2

Figure 2.4 $^1$H-NMR spectra of (a) azide-terminated PVDF$^{18}$ in acetone-$d_6$, (b) alkyne-terminated PLLA$^3$ in CDCl$_3$ and (c) L$_{14}$V$_{72}$L$_{14}^{25}$ block copolymer in acetone-$d_6$. Signals corresponding to PVDF and PLLA are designated with “V” and “L” respectively. Remaining peaks correspond to the NMR solvents.

Figure 2.5 FTIR spectra of (a) bromine-terminated PVDF$^{18}$, (b) azide-terminated PVDF$^{18}$, (c) alkane-terminated PLLA$^3$, (d) alkyne-terminated PLLA$^3$ and (e) L$_{14}$V$_{72}$L$_{14}^{25}$ block copolymer.

To introduce the desired azide functionality onto PVDF, bromine-terminated PVDF (2) was reacted with NaN$_3$ (Scheme 2.1). Figure 2.4a presents the $^1$H-NMR spectrum of the resulting azide-terminated PVDF (3), in which the peaks corresponding to PVDF protons are marked with “V”. A clear upfield shift of the $^1$H-NMR singlet from 4.76 to 4.67 ppm (Figure 2.3a,b) attributed to the methylene
protons, designated with “M”, is observed, indicating the full conversion from bromine to azide end-groups. Additional evidence for azide formation is the appearance of the characteristic absorption band at 2111 cm\(^{-1}\) in the FTIR spectrum assigned to N=N=N stretch vibrations\(^{[25,60]}\) (Figure 2.5a,b).

![GPC traces of alkyne-terminated PLLA\(^3\) in THF (top) and azide-terminated PVDF\(^{18}\) in DMF (bottom).]

**Figure 2.6** GPC traces of alkyne-terminated PLLA\(^3\) in THF (top) and azide-terminated PVDF\(^{18}\) in DMF (bottom).

![Maldi-ToF spectrum of alkyne-terminated PLLA\(^3\). Sodium ions were used for cationization.]

**Figure 2.7** Maldi-ToF spectrum of alkyne-terminated PLLA\(^3\). Sodium ions were used for cationization.
Contrary to the 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 VDF generally results in well-defined products. Consequently, for the synthesized PVDF a polydispersity of 1.21 and number average molecular weight ($M_{n,GPC}$) of 18.3 kg·mol$^{-1}$ was determined by GPC (Figure 2.6), confirming the controlled behavior of this radical VDF polymerization. In agreement with these values, end-group analysis based on the $^1$H-NMR spectrum, comparing the VDF backbone protons with the terminal aromatic protons, revealed a $M_{n,NMR}$ of 19.1 kg·mol$^{-1}$. The polymer will be referred to as PVDF$^{18}$, where the superscript indicates the molecular weight in kg·mol$^{-1}$ measured by GPC.

End-capped PLLA with an acetylene functionality (4) has been prepared via a similar strategy as reported for ROP of ε-caprolactone.$^{[53]}$ Bulk ROP of L-lactide catalyzed by Sn(Oct)$_2$ was performed using hexynol as initiator (Scheme 2.1). In this way, a library of alkyne-terminated PLLA has been prepared (Table 2.1) by altering the ratio between monomer (M) and initiator (I). The molecular weight determined from the GPC curve ($M_{n,GPC}$) (Figure 2.6) is in excellent agreement with the theoretical predicted molar mass ($M_{n,theor}$) (Table 2.1) calculated from the [M]/[I] ratio. The low polydispersity ($PDI$) ranging from 1.05-1.13 indicates the controlled character of this ROP.

The characteristic peaks for the PLLA backbone, designated with “L”, and end-groups (assigned in the experimental section) are represented in the $^1$H-NMR spectrum of PLLA$^3$ (Figure 2.4b). According to the 1:1 integral ratio of –C≡C–H (1.96 ppm) and – CH(CH$_3$)OH (4.35 ppm) end-groups, each polymer chain contains an alkyne functionality. These findings were supported by the Maldi-ToF mass spectrum (Figure 2.7). The observed spacing between adjacent signals equals 144 g·mol$^{-1}$, the mass of one L-lactide unit. The second distribution of lower intensity corresponds to $(n + 1/2)$ repeating units as a result of intermolecular transesterifications, that occur to a certain extent in ROP in the melt above 120 °C.$^{[61]}$ The initiator rest of 98 g·mol$^{-1}$ equals the molar mass of hexynol and therefore confirms the presence of the acetylene end-group. Moreover, the FTIR spectrum (Figure 2.5d) displays a characteristic band at 3290 cm$^{-1}$ attributed to the terminal alkyne.$^{[25,60]}$ ROP of LLA with hexanol, instead of hexynol, led to PLLA
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers without alkyne end-group, and the corresponding spectrum (Figure 2.5c) consequently lacks the signal for C≡C–H stretch vibration. The click reaction between alkyne-terminated PLLA and azide-terminated PVDF was performed to obtain PLLA-b-PVDF-b-PLLA copolymers (5), as pointed out in Scheme 2.1. The recorded $^1$H-NMR spectrum of the final product (Figure 2.4c) reveals the expected signals corresponding to the PVDF and PLLA backbones. Additional analysis of the initial end-groups demonstrated a downfield shift from 4.67 to 5.75 ppm for the methylene proton (Figure 2.3b,c; designated with “M”), indicating successful formation of the triazole ring during the coupling step. In fact, the singlet at 7.83 ppm, marked with a “T”, can be assigned to the triazole proton itself. Consequently, the resonance from the alkyne moiety at 1.96 ppm, observed in the spectrum of PLLA$^3$, disappeared. Further evidence for triazole formation was obtained from the FTIR spectra presented in Figure 2.5, by monitoring the disappearance (Figure 2.5e) of the terminal azide (2111 cm$^{-1}$) and alkyne (3290 cm$^{-1}$) signals present in the end-functionalized homopolymers (Figure 2.5b,d respectively). The CuAAC of PVDF$^{18}$ with PLLA$^3$, PLLA$^9$ and PLLA$^{12}$ led to the formation of three distinct double-crystalline triblock copolymers (Table 2.2). Molar mass determination with GPC in DMF or THF was unsuccessful due to aggregation of the block copolymers in the columns. The expected number average molecular weight ($M_n$) and weight fraction of PLLA ($f_{\text{PLLA}}$) however can be calculated from the predetermined $M_n$ of both homopolymers. To distinguish the synthesized copolymers, we use subscript to indicate the composition in weight percentage and superscript to designate the molecular weight. For instance, L$_{14}$V$_{72}$L$_{14}$$^{25}$ corresponds to a triblock copolymer with a PLLA (L) weight fraction of 0.28, PVDF (V) weight fraction of 0.72, and total molecular weight of 25 kg·mol$^{-1}$.

2.3.2 Structure and crystallization
The crystallization behavior of the synthesized triblock copolymers was examined by studying their thermal behavior and morphology. The behavior of L$_{29}$V$_{42}$L$_{29}$$^{43}$, L$_{24}$V$_{52}$L$_{24}$$^{36}$ and L$_{14}$V$_{72}$L$_{14}$$^{25}$ was investigated in comparison to their respective homopolymers and homopolymer blends. For the latter, bromine-terminated PVDF and alkane-terminated PLLA were used. The lack of reactive (alkyne and azide) end-groups excludes potential reactivity when heating above melting point during analysis.
Figure 2.8 displays the DSC crystallization curves of PVDF and PLLA homopolymers, the corresponding homopolymer blend and \( L_{24}V_{52}L_{24}^{36} \) triblock copolymer. PVDF\(^{18}\) and PLLA\(^{9}\) demonstrate a \( T_c \) of 146 and 114 °C respectively (Figure 2.8a,b). Their crystallization temperatures and degrees of crystallization are listed in Table 2.3, together with the values for the remaining PLLA homopolymers: PLLA\(^{3}\) and PLLA\(^{12}\). Two separated crystallization peaks are observed for the PVDF\(^{18}/PLLAs\) blend and \( L_{24}V_{52}L_{24}^{36} \) copolymer (Figure 2.8c,d), indicating the sequential crystallization of PVDF and PLLA. The \( T_c \) of PLLA in the block copolymer increased considerably (from 114 to 125 °C) in comparison to its parent PLLA homopolymer (Table 2.3). This behavior may be interpreted as a strong nucleation effect caused by the already crystallized PVDF block. The crystallization temperature of the PVDF block on the other hand showed a slight depression compared to the respective homopolymer. Similar behavior is observed for the homopolymer blend, in which the \( T_{c,PLLAs} \) even increased up to 129 °C.
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers

Table 2.3 Crystallization of homopolymers, homopolymer blends and block copolymers.

<table>
<thead>
<tr>
<th>Product \textsuperscript{a}</th>
<th>PLLA</th>
<th></th>
<th>PVDF</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_c$ \textsuperscript{b} (°C)</td>
<td>$X_c$ \textsuperscript{c} (%)</td>
<td>$T_c$ \textsuperscript{b} (°C)</td>
<td>$X_c$ \textsuperscript{c} (%)</td>
</tr>
<tr>
<td>PVDF\textsuperscript{18}</td>
<td>108</td>
<td>49</td>
<td>146</td>
<td>59</td>
</tr>
<tr>
<td>PLLA\textsuperscript{3}</td>
<td>114</td>
<td>51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLLA\textsuperscript{9}</td>
<td>114</td>
<td>53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLLA\textsuperscript{12}</td>
<td>113</td>
<td>46</td>
<td>140</td>
<td>59</td>
</tr>
<tr>
<td>PVDF\textsuperscript{18}/PLLA\textsuperscript{3}</td>
<td>129</td>
<td>54</td>
<td>142</td>
<td>43</td>
</tr>
<tr>
<td>PVDF\textsuperscript{18}/PLLA\textsuperscript{9}</td>
<td>129</td>
<td>55</td>
<td>140</td>
<td>38</td>
</tr>
<tr>
<td>PVDF\textsuperscript{18}/PLLA\textsuperscript{12}</td>
<td>125</td>
<td>29</td>
<td>141</td>
<td>62</td>
</tr>
<tr>
<td>L\textsubscript{14}V\textsubscript{25}L\textsubscript{14} \textsuperscript{25}</td>
<td>128</td>
<td>42</td>
<td>140</td>
<td>60</td>
</tr>
<tr>
<td>L\textsubscript{24}V\textsubscript{52}L\textsubscript{24} \textsuperscript{36}</td>
<td>128</td>
<td>42</td>
<td>140</td>
<td>60</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Bromine-terminated PVDF and alkane-terminated PLLA were used for measurement of homopolymers and blends. The lack of reactive (alkyne and azide) end-groups excludes potential reactivity when heating above melting point during analysis. \textsuperscript{b} Determined from DSC thermograms. \textsuperscript{c} Calculated using the following equation: $X_c = (\Delta H_c/(f \cdot \Delta H_{100})) \cdot 100\%$. $\Delta H_{c,PVDF}$ and $\Delta H_{c,PLLA}$ were determined from DSC thermograms, $f_{PVDF}$ and $f_{PLLA}$ are derived from Table 2.2, $\Delta H_{100,PVDF} = 104.5 \text{ J/g}$ and $\Delta H_{100,PLLA} = 93.0 \text{ J/g}$.[62]

The degree of crystallization ($X_c$) for all samples was calculated from the crystallization enthalpy (Table 2.3), taken into consideration the enthalpy for fully crystallized PLLA and PVDF (and the block fraction in case of block copolymer samples). The $X_c$ of the PLLA block within the block copolymer was strongly depressed (i.e. 22%) with respect to PLLA homopolymer. This again confirms the influence of PVDF over PLLA crystallization. PLLA domains are confined, i.e. trapped, within the crystalline PVDF matrix, and consequently the crystallization of the lower temperature block is hindered. Similar depressions were observed in PLLA-b-PEO block copolymer systems.[17] On the other hand, the PVDF\textsuperscript{18}/PLLA\textsuperscript{9} blend demonstrated a similar degree of PLLA crystallization as the parent PLLA homopolymer. Within the blend, PLLA is not trapped in the PVDF matrix, and its crystallization is not influenced by the higher temperature block apart from the above described nucleation effect. The degree of crystallization of the PVDF block is not different from the homopolymer, witnessed by similar values for the $X_c,PVDF$.
(Table 2.3). PVDF crystallizes first from the melt, and its crystallization is apparently hardly influenced by the molten PLLA blocks, apart from the slight depression of $T_c$.

**Figure 2.9** WAXS patterns of (a) PVDF$^{18}$ homopolymer, (b) PLLA$^{9}$ homopolymer and (c) $L_{24}V_{52}L_{24}^{36}$ triblock copolymer recorded at room temperature after crystallization from the melt.

**Figure 2.10** WAXS patterns of (a) $L_{24}V_{52}L_{24}^{36}$ cast from DMF solution and (b) $L_{24}V_{52}L_{24}^{36}$ crystallized from the melt.
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers

Figure 2.11 2D-WAXS pattern of L$_{24}$V$_{52}$L$_{36}$ triblock copolymer recorded at room temperature after crystallization from the melt.

The crystallinity of both blocks was confirmed by wide-angle X-ray experiments. Figure 2.9 compares the WAXS intensity profile of L$_{24}$V$_{52}$L$_{36}$ copolymers with that of PVDF$^{18}$ and PLLA$^9$ homopolymers, recorded after crystallization from the melt. Both characteristic PVDF and PLLA reflections (Figure 2.9a,b) are visible in the block copolymer sample (Figure 2.9c). For example, the intense scattering peak at $q = 11.8$ nm$^{-1}$ corresponds to the (110) and (200) reflections of PLLA. The signal at 14.1 nm$^{-1}$ is attributed to the (110) crystal plane of α-phase PVDF. The non-polar α-polymorph of PVDF is formed during crystallization from the melt (Figure 2.10a). However, the polar β-crystalline phase, known for its piezo- and ferroelectric behavior, was initially formed after solvent-casting from DMF solution, confirmed by the presence of the characteristic (110)/(200) reflections of β-phase PVDF at 14.3 nm$^{-1}$ (Figure 2.10b). The 2-dimensional scattering pattern of the double-crystalline block copolymer at wide-angle, depicted in Figure 2.11, reveals the large amount of reflections arising from both crystallized blocks.

The resulting superstructures of isothermally crystallized PVDF and PLLA homopolymers, PVDF$^{18}$/PLLA$^9$ blend and L$_{24}$V$_{52}$L$_{36}$ block copolymer are depicted in Figure 2.12. Both homopolymers present a clear spherulitic microstructure between crossed polarizers (Figure 2.12a,b), with the typical Maltese cross in the birefringence pattern. As expected, the homopolymer blend reveals a macrophase separated system consisting of both PVDF and PLLA domains (Figure 2.12c). Contrary, the optical micrograph of L$_{24}$V$_{52}$L$_{36}$ (Figure 2.12d) demonstrates a single spherulitic microstructure comparable to its parent homopolymers. Similar superstructures were observed for isothermally crystallized double-crystalline PLLA-b-PCL copolymers,$^{16}$ and indicate crystallization from a homogeneous or weakly segregated melt. When stronger thermodynamic segregation between the blocks is present, the phenomenon of break-out is more difficult and more distorted microstructures are obtained,$^{11,21}$ as observed in Chapter 3.
Figure 2.12 POM images of (a) PVDF\textsuperscript{18} isothermally crystallized at 145 °C, (b) PLLA\textsuperscript{9} isothermally crystallized at 125 °C, (c) PVDF\textsuperscript{18}/PLLA\textsuperscript{9} blend isothermally crystallized at 145 °C and (d) L\textsubscript{24}V\textsubscript{52}L\textsubscript{24} \textsuperscript{36} block copolymer isothermally crystallized at 145 °C. All images were recorded at room temperature.

A miscible melt system was observed for L\textsubscript{24}V\textsubscript{52}L\textsubscript{24} \textsuperscript{36} (and all other block copolymer samples) during temperature-resolved small-angle X-ray experiments (Figure 2.13b). Such a single phase in the melt is observed for crystalline-amorphous PVDF-containing block copolymers as well (Chapter 4 and 5). Upon cooling from the homogeneous melt, microphase separation occurs driven by crystallization. Hence, the SAXS intensity profile of L\textsubscript{24}V\textsubscript{52}L\textsubscript{24} \textsuperscript{36} recorded at room temperature (Figure 2.13a), after crystallization from the melt, reveals a diffraction pattern with a $q$ ratio of 1:2. The integer ratio of $q$ at the scattering maxima indicates a lamellar morphology. Since structure formation in the sample is driven by crystallization, the nanostructure most probably consists of alternating crystalline PVDF and PLLA domains. The lamellar domain spacing of 24 nm was calculated from the first-order reflection at $q^* = 0.26$ nm$^{-1}$. TEM experiments confirm the lamellar nanostructure of the block copolymer (Figure 2.14), and the observed length scale corresponds with the calculated domain spacing.
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers

Figure 2.13 SAXS patterns of $L_{24}V_{52}L_{24}^{36}$ triblock copolymer recorded (a) at 25 °C after crystallization from homogeneous melt and (b) in the melt state at 200 °C.

Figure 2.14 Bright-field TEM image of the lamellar nanostructure in $L_{24}V_{52}L_{24}^{36}$ triblock copolymer.
Figure 2.15 DSC crystallization curves of (a) L$_{29}$V$_{42}$L$_{29}$, (b) L$_{24}$V$_{52}$L$_{24}$ and (c) L$_{14}$V$_{72}$L$_{14}$ triblock copolymers obtained during cooling from the melt with 10 °C/min. The inset in (c) demonstrates the fractionated crystallization of L$_{14}$V$_{72}$L$_{14}$.

In Figure 2.15, DSC cooling scans of all three synthesized PLLA-b-PVDF-b-PLLA copolymers are compared. The crystallization temperature and degree of crystallization of the PVDF component remain constant, with values around 140 °C and 60% respectively (Table 2.3). On the other hand, the crystallization behavior of the PLLA block depends strongly on the block composition. The $T_{c,PLLA}$ of L$_{29}$V$_{42}$L$_{29}$ triblock copolymer with PLLA content up to 58% is determined to be 128 °C (Figure 2.15a). The crystallization temperature of the lower temperature block has increased significantly compared to that of the respective PLLA homopolymer, supposedly due to a nucleation effect caused by the PVDF phase. Similar results were already discussed for L$_{24}$V$_{52}$L$_{24}$ (Figure 2.8d = Figure 2.15b). Contrary, a very strong depression of $T_{c,PLLA}$ is found in the L$_{14}$V$_{72}$L$_{14}$ triblock copolymer (Figure 2.15c, inset), in which PLLA is the minor block with a content of only 27%. This fractionated crystallization is a consequence of confined crystallization of the PLLA component within the previously formed PVDF matrix, and has been encountered before for various other double-crystalline block copolymer systems.$^{[12,15]}$ When the PLLA fraction is low enough, PLLA chains are confined to crystallize within the
Sequential crystallization of PLLA-b-PVDF-b-PLLA copolymers

separately nanoscopic scale between the crystalline PVDF lamellae. Consequently, PLLA crystallization occurs at large supercooling, i.e. 85 °C (Table 2.3).

Considering the degree of crystallization, all block copolymer samples demonstrate a decrease of $X_{c,PLLA}$ values with respect to their parent homopolymers PLLA$^3$, PLLA$^9$ and PLLA$^{12}$ (Table 2.3), indicating the influence of crystallized PVDF that hinders the PLLA crystallization. The effect is most pronounced for L$_{14}$V$_{72}$L$_{14}^{25}$, containing the lowest content of PLLA, in which a very large depression up to 39% is obtained. The observed trend with composition further confirms the role of confinement upon PLLA crystallization. In contrast, the degree of PVDF crystallization is constant with composition (Table 2.3). Supposedly, the crystallization of the higher temperature block is not influenced by the molten PLLA chains, regardless of their length.

![Figure 2.16 WAXS patterns](image)

**Figure 2.16** WAXS patterns of (a) L$_{24}$V$_{52}$L$_{24}^{36}$ and (b) L$_{14}$V$_{72}$L$_{14}^{25}$ triblock copolymers as function of temperature during cooling from the melt with 10 °C/min.

Temperature-resolved WAXS experiments were performed to further investigate the crystallization of both blocks from the melt, since this is known to be a valuable method to assign DSC peaks to the corresponding crystalline components. Equal to DSC analysis, cooling rates of 10 °C/min were employed. Figure 2.16a displays WAXS patterns of L$_{24}$V$_{52}$L$_{24}^{36}$ as function of temperature during cooling from 180 to 60 °C. Complementary to the DSC curve in Figure 2.15b, crystallization of PVDF occurs at 140 °C, while PLLA starts to crystallize at 125 °C, confirming the sequential crystallization of both blocks. On the other hand, crystallization of the lower temperature PLLA block in the L$_{14}$V$_{72}$L$_{14}^{25}$ copolymer
occurs at large supercooling around 85 °C according to the temperature-resolved WAXS intensity profiles in Figure 2.16b. These results confirm the fractionated crystallization phenomenon observed in the DSC cooling scan (Figure 2.15c). Furthermore, the low intensity of the characteristic PLLA scattering peak at $q = 11.8 \text{ nm}^{-1}$ confirms the low degree of crystallization of the PLLA block for this particular triblock copolymer sample.

Figure 2.17 POM images during isothermal crystallization: (a) $L_{29}V_{42}L_{29}$ after 5 min at 145 °C, (b) $L_{29}V_{43}L_{29}$ after 5 min at room temperature, (c) $L_{24}V_{52}L_{24}$ after 5 min at 145 °C, (d) $L_{24}V_{52}L_{24}$ after 5 min at room temperature, (e) $L_{14}V_{72}L_{14}$ after 5 min at 145 °C and (f) $L_{14}V_{72}L_{14}$ after 5 min at room temperature.
To study the formation of the block copolymer microstructure with POM in more detail, $L_{29}V_{42}L_{29}^{43}$, $L_{24}V_{52}L_{24}^{36}$ and $L_{14}V_{72}L_{14}^{25}$ were isothermally crystallized at 145 °C between crossed polarizers (Figure 2.17a,c,e respectively), allowing crystallization of the higher temperature PVDF block only. $L_{29}V_{42}L_{29}^{43}$ revealed a disordered crystalline structure (Figure 2.17a), supposedly due to the large content of molten PLLA, hindering the formation of ordered spherulites. On the other hand, clear spherulitic superstructures were observed for $L_{24}V_{52}L_{24}^{36}$ and $L_{14}V_{72}L_{14}^{25}$ (Figure 2.17c,e). At 145 °C, the spherulites are most probably composed of PVDF crystalline lamellae and interlamellar regions consisting of a mixture of PVDF and PLLA chains in the amorphous state. Subsequently, the temperature was lowered to room temperature, and PLLA crystallization occurred (Figure 2.17b,d,f). The morphology remains invariable during crystallization of the lower temperature block, as PLLA crystallizes in a confined fashion within the interlamellar regions of the previously formed PVDF spherulites that act as template. As a result, only changes in the degree of brightness and color are obtained in the birefringence pattern of $L_{29}V_{42}L_{29}^{43}$ and $L_{24}V_{52}L_{24}^{36}$ (Figure 2.17b,d respectively). Similar results have been reported for PLLA-\textit{b}-PCL diblock copolymers.\textsuperscript{[16]} On the other hand, no clear change can be observed in the optical micrograph of $L_{14}V_{72}L_{14}^{25}$ after PLLA crystallization (Figure 2.17f). DSC and WAXS experiments already indicated a very low degree of crystallization for the lower temperature block in this sample (respectively in Figure 2.15c and Figure 2.16b), and the effect is apparently too small to be observed in POM.

### 2.4 Conclusion

The preparation and crystallization of poly(L-lactide)-\textit{block}-poly(vinylidene fluoride)-\textit{block}-poly(L-lactide) copolymers, composed of two crystallizable components, has been discussed. The synthesis route towards this product involved ring opening polymerization of L-lactide, benzoyl peroxide initiated polymerization of vinylidene fluoride, and subsequential “clicking” of the tailored PLLA and PVDF performing copper(I)-catalyzed azide-alkyne cycloaddition. As a result, three distinct triblock copolymers having different block ratios were successfully prepared.

The double-crystalline block copolymers form a single phase in the melt, however upon cooling microphase separation driven by crystallization leads to an ordered
lamellar morphology at the nanoscale. The β-polymorph of PVDF, well-known for its ferroelectric and piezoelectric properties, was initially observed in the block copolymer films after solvent-casting from DMF, while the α-phase was obtained when crystallized from the melt.

Two separated crystallization temperatures were obtained due to the sequential crystallization of PVDF and PLLA. The crystallization behavior of the lower temperature crystallizing PLLA was strongly influenced by the block composition. The crystallization temperature of the PLLA block increased considerably for rather symmetric block copolymers (49 and 58% PLLA) compared to the respective homopolymers, indicating a nucleation effect caused by the crystallized PVDF phase. Contrary, a tremendous depression of $T_{c,PLLA}$ was observed for asymmetric block copolymers with minor PLLA content (27%), due to a confined crystallization process referred to as fractionated crystallization. The degree of crystallization of PLLA was significantly decreased in all block copolymers with respect to the parent PLLA homopolymers, indicating the influence of the crystallized PVDF phase that traps (i.e. confines) the crystallization of the lower temperature block. In contrast, crystallization of the PVDF block was hardly influenced, demonstrated by the constant values of $T_{c,PVDF}$ and $X_{c,PVDF}$. The confined crystallization of PLLA was confirmed by microstructural analysis during isothermal crystallization. PLLA crystallizes within the interlamellar regions of the preformed PVDF spherulites. The morphology obtained during PVDF crystallization remains therefore identical upon crystallization of PLLA at lower temperatures.

PLLA-b-PVDF-b-PLLA copolymers may be used as precursors to prepare well-ordered nanoporous PVDF by selective removal of the PLLA blocks. Resulting PVDF nanofoams can demonstrate strong piezoelectricity and may find application in loudspeakers, keypads and hydrophones.

2.5 References

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