Bioinspired All-Polyester Diblock Copolymers Made from Poly(Pentadecalactone) and Poly(3,4-Ethylene Furanoate): Synthesis and Polymer Film Properties

Julia S. Saar and Karen Lienkamp*

Bio-based, fully degradable aliphatic-aromatic block copolymers are synthesized from ω-pentadecalatone and cyclic oligo(3,4-ethylene furanoate). In the first approach, the ring-opening polymerization of the cyclic oligo(3,4-ethylene furanoate) is initiated by a poly(pentadecalactone) macroinitiator with a terminal hydroxy group. The reaction temperatures of the melt polymerization are 210–230 °C due to the high melting points of the oligo(3,4-ethylene furanoate). Under these conditions, transesterification is observed. The blockiness of the reaction products depends on the reaction temperature and on the ratio of pentadecalactone to 3,4-ethylene furanoate repeat units, which is 50:50, 80:20, and 90:10. At lower temperatures and more pentadecalactone content, the blockiness is larger. The number average molar mass of the block copolymers remains smaller than 20 000 g mol^{-1}. In the second approach, poly(pentadecalactone) is functionalized with an alkyne group, and the OH group of the oligo(3,4-ethylene furanoate) (molar mass 1900 g mol^{-1}) is converted into an azide group. Connecting the two polymers in a copper-catalyzed 1,3-dipolar addition reaction ("click reaction") yields block copolymers with a number average molar mass of 12 400 g mol^{-1}. The mechanical properties of the polymer films are intermediate between those of the parent homopolymers.

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1. Introduction

Poly(ethylen terephthalate) (PET) is a fossil fuel-based thermoplastic polymer that is widely used in the packaging industry and as fibers thanks to its transparency, high tensile strength, and dimensional stability. One of the best-known applications are PET bottles, for which well-working recycling concepts have been established. Unfortunately, PET not disposed of properly continues to contaminate the environment and thereby contributes to microplastics accumulation on land and in waterways. Although a polyester, PET does not biodegrade well due to its overall hydrophobicity and semicrystallinity. In recent years, biomass-based poly(ethylene furanoate) (PEFs) have been discussed as an alternative for PET. PEFs can be obtained by polycondensation of furane dicarboxylic acids (FDCAs) or their ester derivatives with a diol. For example, Thiyagarajan et al. describe the reaction of the 2,5-, 2,4-, and 3,4-furane dimethyldicarboxylates with different diols via melt polycondensation.[1] FDCAs are obtained via the Henkel reaction, a thermal disproportionation reaction in which the alkali salts of furane-2-carboxylic acid form a mixture of the corresponding dicarboxylate and the unsubstituted furane.[2] The main product of this reaction are the 2,5-dicarboxylate and the 2,4-dicarboxylate, while the 3,4-dicarboxylate forms as a byproduct (about 5%).[2] When reacting the purified dicarboxylate isomers with ethylene glycol, PEFs with number-average molar masses (M_n) of 36 000–65 000 g mol^{-1} and dispersity values between 1.5 and 2.5 were obtained,[1] which is a useful range for thermoplastic materials (i.e., above the entanglement molar mass). The symmetric 2,5- and 3,4-isomers yield semicrystalline polymers, while the polymerization product of the asymmetric 2,4-isomer is amorphous.[1] Another possibility to obtain PEFs is the ring-opening polymerization of cyclic oligo(ethylen furane dicarboxylates) (cyc-OEFs).[3,4] Previous research has shown that this reaction type offers better control over the obtained molar mass and dispersity than polycondensation, which is important in the context of the expected materials properties.[3] Like PET, poly(ethylen-2,5-furane dicarboxylate) has very good gas barrier properties (gas permeabilities: PET: 0.114 Barrer at 35 °C for O$_2$, 0.49 Barrer at 35 °C for CO$_2$; PEF: 0.011 Barrer at 35 °C for O$_2$, 0.026 Barrer at 35 °C for CO$_2$)[5] and at the same time good

mechanical properties, so that it is expected to replace PET in a number of products.[6]

Another interesting polymer that can be obtained from renewable resources is poly(ω-pentadecalactone) (PPDL),[7] which resembles polyethylene (PE). Like PET, PE is nondegradable and, being the polymer most often used in packaging, plays a major role in environmental pollution. Thus, its replacement by degradable alternatives would be desirable. The monomer for PPDL, ω-pentadecalactone, is widely used in the fragrance industry, with an estimated annual production volume of 10–1000 metric tons worldwide already.[8] In previous work, we have investigated block copolymers made from PPDL with 3-hydroxycinnamic acid and poly(2-(2-hydroxyethoxy) benzoate) as fully degradable aliphatic-aromatic phase compatibilizers.[9,10] The aim of the here presented work was to synthesize all bio-based, fully degradable block copolymers from PPDL and poly(ethylen-3,4-furane dicarboxylate), also with potential use as an all-degradable phase compatibilizer for either bio-based PPDL-PEF blends, or as an additive for recycled fractions of PE with PET or other polymeric impurities. Without such phase compatibilization, even small amounts of impurities are well known to be detrimental for the mechanical properties of the recycled material.[11] While other authors focused on the 2,5- and 2,4-isomers of PEF in their research, we deliberately used in the 3,4-isomer to demonstrate that this byproduct can also find useful materials applications. Since both cyclic oligo(ethylene furane dicarboxylate) and ω-pentadeclactone polymerize by ring-opening polymerization, in a first approach we attempted using PPDL as a macroinitiator for the initiation of cyc-OEF (**Scheme 1**). This approach was successful in previous research when synthesizing poly(tetrahydrofurane-block-PET) from tetrahydrofuran and cyclic oligoethylene terephthalate.[12] As an alternative, the synthesis of end-functionalized PPDL and PEF homopolymers, followed by their connection to a block copolymers via polymer-analogous reactions is presented.

2. Experimental Section

2.1. Materials

All chemicals were obtained as reagent grade from Sigma-Aldrich (St. Louis, MO), Carl Roth (Karlsruhe, Germany), or Alfa Aeser (Haverhill, MA) and used as received. High performance liquid chromatography (HPLC) grade solvents were purchased dry from Carl Roth and used as received. ω-Pentadecalactone (PDL) was sublimated and dried under high vacuum for 3 days. Propargyl alcohol (PA) and benzyl alcohol (BA) were dried over calcium hydride and distilled under reduced pressure. Azidopropanol (AP) was distilled under reduced pressure. Triazabicyclodecene (TBD) was recrystallized from diethyl ether and dried under high vacuum for 3 days. Toluene, chloroform, PDL, PA, BA, and TBD were stored and handled under nitrogen in a glovebox (MBRAUN, Garching, Germany).

2.2. Instrumentation

Gel permeation chromatography (GPC, in chloroform, calibrated with poly(methyl methacrylate) and polystyrene standards) was performed on PSS SDV 100, 1000, and 10 000 Å columns (PSS, Mainz, Germany) using a 1260 Infinity RI detector (Agilent Technologies, Santa Clara, CA). GPC measurements for poly(ethylene-3,4-furandicarboxylate) were conducted in hexafluoroisopropanol with 0.02 M potassium trifluoroacetate using two PFG linear M columns (PSS, Mainz, Germany), an Agilent 1100 variable wavelength detector/ultraviolet (VWD/UV) detector (Santa Clara, CA), a DAWN HELEOS II MALS detector and an Optilab T-rEX RI detector (Santa Barbara, CA). To evaluate the data, PET standards were used. NMR spectra were recorded on a Bruker (Billerica, MA) 250 MHz spectrometer using CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal reference. Fourier-transform infrared spectroscopy (FTIR) spectra were taken using a Cary 630 FTIR Spectrometer (Agilent Technologies, Santa Clara, CA). The glass transition temperature and melting temperature were measured by differential scanning calorimetry (DSC). The thermograms were recorded on a Phönix DSC 204 F1 device (Netzsch, Selb, Germany) in a temperature range of -20–250 °C and with a speed of 5 K min^{-1}. MALDI-TOF mass spectrometry measurements were conducted using an autoflexTOF/TOF (Bruker, Billerica, MA) with *trans*-2-[3-(4-*tert*-butylphenyl)$-$2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix material. Silver or sodium was used for the ionization. Mass spectrometry with electrospray ionization (ESI) was used to analyze the cyclic monomers and was performed with a device from Thermo Fisher Scientific (Waltham, MA).

For the formation of polymeric layers on silicon wafers, a SPIN150 spin coater (SPS-Europe, Putten, Netherlands) was used with the following process parameters: 3000 rpm, 1000 rpm s^{-1}, and 30 s spinning time. The thickness of the polymer layers was measured with a SE400adv ellipsometer (Sentech Instruments GmbH, Berlin). The static, advancing, and receding contact angles were measured by using OCA 20 contact angle measurement set-up (Data Physics GmbH, Filderstadt, Germany). For each sample, the average value from three different positions was taken. Atomic force microscopy (AFM) was used to analyze the surface topology. A Dimension Icon AFM from Bruker (Billerica, MA) was used. RFESP-75 (width: 40 µm, length: 235 µm, spring constant: 4.18 N m^{-1}, resonance frequency: 76 kHz) as well as ScanAsyst-Air (width: 25 µm, length: 115 µm, spring constant: 0.4 N m^{-1}, resonance frequency: 70 kHz) cantilevers were used. In order to perform Quantitative Nanomechanical (PeakForce-QNM) measurements, the deflection sensitivity, the spring constant, and the tip radius were calibrated prior to use. A sapphire standard sample from Bruker (PFQNM-SMPKIT-12 M, SAPPHIRE-12 M) was used to calibrate the deflection sensitivity, which resulted in 94.96 nm V^{-1} for the ScanAsyst-Air cantilever and 125.92 nm V^{-1} for the RFESP-75. The spring constant for the ScanAsyst-Air cantilever was calibrated using thermal tune, which resulted in a value of 0.463 N m^{-1}. The spring constant of the RFESP-75 was calculated using the Sader method,[13] which resulted in a value of 4.18 N m^{-1}. In order to determine the tip radius, an absolute method was used. A titanium carbide standard sample from Bruker (PFQNM-SMPKIT-12 M, RS-12 M) was used to perform a Tip Check. Then, the titanium carbide sample was replaced by one of the samples. Using the titanium carbide sample, the value of the PeakForce (PF) setpoint was manually adjusted to obtain a 2 nm surface deformation. The curve of force (in nN) versus
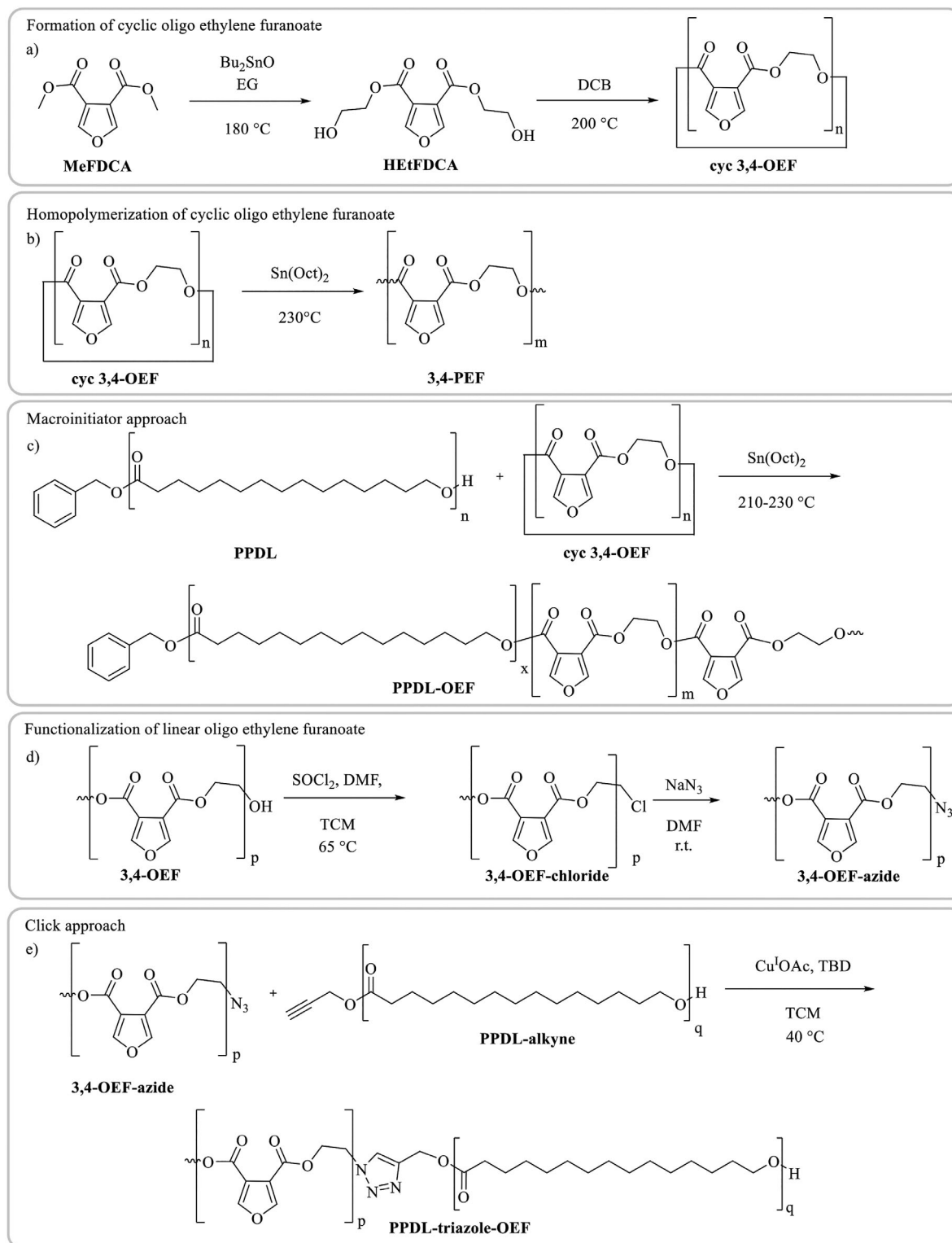
Scheme 1. a) Dimethyl furan-3,4-dicarboxylate (**MeFDCA**) was first converted into bis(2-hydroxyethyl) furane-3,4-dicarboxylate (**HEtFDCA**) using ethylene glycol. In the second step, cyclic oligoethylene furanoate (**cyc 3,4-OEF**) was synthesized. b) **cyc 3,4-OEF** was polymerized to yield poly(ethylene-3,4-furandicarboxylate) (**PEF**). c) Macroinitiator approach: poly(pentadecalactone) (**PPDL**) was used as a macroinitiator for the polymerization of **cyc 3,4-OEF**, which gave the statistical copolymer **PPDL-OEF**. d) Functionalization of linear oligoethylene furanoate (**3,4-OEF**) with azide groups, yielding **3,4-OEF-azide**. e) Click approach: **3,4-OEF-azide** was linked to alkyne-functionalized PPDL (**PPDL-alkyne**) using a copper catalyzed azide-alkyne cycloaddition, which yielded the block copolymers **PPDL-triazole-OEF**. Bu$_2$SnO: dibutyltin oxide; EG: ethylene glycol, Sn(Oct)$_2$: dioctyltin; DMF: *N,N*-dimethylformamide; TCM = trichloromethane, TBD = triazabicyclodecene.

z position (in nm) was captured and the indentation depth was measured using the Nanoscope Analysis 1.5 software. The value of the indentation depth was inserted into the tip check image of the titanium carbide standard sample to calculate the tip radius. The RFESP-75 tip used for the PPDL sample had a tip radius of 6.05 nm, the one used for the PPDL-triazole-OEF sample had a radius of 3.81 nm. For the ScanAsyst-Air tip used for the PEF sample, the tip radius was 11.3 nm.

2.3. Synthesis

2.3.1. Synthesis of Cyclic Oligoethylene Furanoate

Dimethyl furan-3,4-dicarboxylate (MeFDCA) (616 mg, 3.35 mmol) was reacted with an excess of ethylene glycol (2.08 g, 1.87 mL, 33.5 mmol) under nitrogen and in the presence of Bu_2SnO (8.33 mg, 0.033 mmol). The reaction was stirred for 5 h at 180 °C. Full conversion of MeFDCA to bis(2-hydroxyethyl) furan-3,4-dicarboxylate (HEtFDCA) was confirmed via proton NMR measurements. Dichlorobenzene (DCB, 70 mL) was added, and the reaction was stirred at 200 °C for 24 h, followed by partially removing DCB and the formed alcohol. The reaction mixture was filtered while still hot to remove solid polymeric species, and was precipitated into cooled pentane (when it was not already precipitating while cooling down). For purification, column chromatography (dichloromethane:ethyl ether in a volume ratio of 9:1, silica gel 60, 15 cm length, 5 cm diameter) was used, resulting in a colorless product, with a yield of 73% and different cyclic species with ring sized between two and seven repeat units.

^{1}H NMR (HEtFDCA, 250 MHz, CDCl$_3$, δ): 8.06 (s, 2H, C$_{aromat}$H), 4.41 (t, J = 4.7 Hz, 2H, CH$_2$), 3.89 (t, J = 4.7 Hz, 2H, CH$_2$-OH); ^{1}H NMR (cyc 3,4-OEF, 250 MHz, CDCl$_3$, δ): 7.97 (s, 2H, C$_{aromat}$H), 4.60 (s, 4H, CH$_2$); ^{13}C NMR (cyc 3,4-OEF, 63 MHz, CDCl$_3$, δ): 161.95, 148.80, 118.00, 62.71; ESI-MS (m/z): 365.05 [C$_{16}$H$_{12}$O$_{10}$H]$^+$, 387.03 [C$_{16}$H$_{12}$O$_{10}$Na]$^+$, 547.07 [C$_{24}$H$_{18}$O$_{15}$H]$^+$, 569.05 [C$_{24}$H$_{18}$O$_{15}$Na]$^+$, 729.09 [C$_{32}$H$_{24}$O$_{20}$H]$^+$, 751.07 [C$_{32}$H$_{24}$O$_{20}$Na]$^+$, 933.09 [C$_{40}$H$_{30}$O$_{25}$Na]$^+$, 1151.11 [C$_{48}$H$_{36}$O$_{30}$Na]$^+$, 1297.13 [C$_{56}$H$_{42}$O$_{35}$Na]$^+$; $T_{m,mixture}$ = 200–215 °C.

2.3.2. Synthesis of Poly(ethylene-3,4-furandicarboxylate)

Poly(ethylene-3,4-furandicarboxylate) (PEF) was synthesized via ring-opening polymerization. Cyclic oligoethylene furanoate (197 mg, 1.08 mmol) and Sn(Oct)$_2$ (3.99 mg, 0.01 mmol) were mixed in a Schlenk tube. Dichloromethane (DCM) was added to fully dissolve and homogenize the reaction mixture. Afterward, DCM was removed, and the reactants were dried overnight under high vacuum. The Schlenk tube was placed in a 230 °C heated oil bath and the reaction was stirred for 1 h. Proton NMR of the crude product revealed complete conversion of the cyclic species into linear ones. The product mixture was dissolved in trifluoracetic acid (TFA) and precipitated into DCM to remove traces of any unreacted cyclic species. The polymer was obtained as a beige solid (95% yield, M_n = 60 000 kg mol^{-1}, Đ = 1.68).

^{1}H NMR (250 MHz, TFA-d, δ): 8.12 (s, 2H, C$_{aromat}$H), 4.67 (s, 4H, CH$_2$); ^{13}C NMR (63 MHz, CDCl$_3$, δ): 167.10, 154.22, 119.27, 66.31.

2.3.3. Synthesis of Block Copolymers Using Poly(pentadecalactone) as Macroinitiator

The syntheses of poly(pentadecalactone) (PPDL) bearing an benzyl alcohol end group was described previously.[14] The characterization data PPDL macroinitiators used can be found the same publication.[14] Cyclic oligoethylene furanoate (37.9 mg, 0.208 mmol ethylene furanoate units), poly(pentadecalactone) (M_n = 2200 g mol^{-1}, 50.0 mg, 0.023 mmol PPDL chains, 0.208 mmol PDL units) and Sn(Oct)$_2$ (0.843 mg, 0.002 mmol) were placed in a Schlenk tube. DCM was added to fully dissolve and homogenize the reactants. Afterward, DCM was removed, and the reactants were dried overnight under high vacuum. The Schlenk tube was put in a preheated oil bath and the reaction was stirred for 1 h. The amount of each reactant as well as the reaction conditions of all reaction batches are listed in **Table 1**. The copolymers were obtained as a dark brown solid.

^{1}H NMR (250 MHz, CDCl$_3$, δ): 7.91-8.05 (m, 2H$_{PEF}$, C$_{aromat}$H), 7.33-7.44 (m, 5H, C$_{aromat,initiator}$H), 5.30 (s, 2H, C$_{initiator}$H$_2$), 5.29 (s, 2H, C$_{initiator}$H$_2$-F), 5.11 (s, 2H, C$_{initiator}$H$_2$-PDL), 4.20-4.60 (m, 4H$_{PEF}$, O-CH$_2$ and 2H$_{PEF}$, CH$_2$-CH$_2$-O$_{ether}$ and 2H$_{PEF}$, CH$_2$-CH$_2$-OH and 2H$_{PPDL}$, O-CH$_2$), 4.05 (t, J = 6.7 Hz, 2H$_{PPDL}$, CH$_2$-O-PDL), 3.84-3.90 (m, 2H$_{PEF}$, CH$_2$-OH), 3.76-3.82 (m, 2H$_{PEF}$, CH$_2$-O$_{ether}$), 3.61-3.69 (m, 2H$_{PPDL}$, CH$_2$-OH), 2.24-2.41 (m, 2H$_{PPDL}$, CH$_2$-C = O), 1.54-1.76 (m, 4H$_{PPDL}$, CH$_2$), 1.19-1.44 (m, 20H$_{PPDL}$, CH$_2$); ^{13}C NMR (63 MHz, CDCl$_3$, δ): 173.97, 173.56, 161.71, 161.45, 161.18, 161.01, 149.44, 149.24, 149.16, 148.95, 148.66, 148.42, 146.04, 128.55, 128.50, 128.31, 128.12, 118.59, 118.53, 118.00, 117.92, 117.86, 117.80, 66.72, 65.17, 64.37, 62.73, 62.47, 61.95, 61.75, 61.71, 34.38, 34.09, 29.61, 29.52, 29.45, 29.25, 29.15, 29.10, 28.63, 28.57, 25.91, 24.99, 24.85.

2.3.4. Functionalization of Linear Oligomeric Ethylene Furanoate

1) Introduction of chloride end groups. During the synthesis of cyclic monomer, linear oligomeric species were formed as a byproduct, with a number-average molar mass of 1900 g mol^{-1}. Those oligomers (127 mg, 0.067 mmol) were dissolved in chloroform and thionyl chloride (24.2 μL, 39.8 mg, 0.334 mmol) with catalytic amounts of DMF (2.59 μL, 2.44 mg, 0.033 mmol). The reaction mixture was stirred under reflux at 65 °C for 4 days. Afterward, the solvent was removed, and the product was washed several times with hexane. Proton NMR revealed full conversion of the hydroxyl end groups to alkyl chloride (87% yield).

Linear 3,4-OEF: ^{1}H NMR (250 MHz, CDCl$_3$, δ): 7.95-8.06 (s, 2H, C$_{aromat}$H), 4.49-4.58 (m, 4H, CH$_2$), 4.34-4.41(m, 2H, CH$_2$-CH$_2$-OH and 2H, CH$_2$-CH$_2$-O$_{ether}$), 3.84 (t, J = 4.74 Hz, 2H, CH$_2$-OH), 3.75-3.80 (m, 2H, CH$_2$-O$_{ether}$); ^{13}C NMR (63 MHz, CDCl$_3$, δ): 161.84, 161.51, 161.11, 161.05, 151.10, 150.80, 150.15, 149.56, 149.53, 149.51, 149.48, 149.36, 118.28, 117.66, 117.64, 117.00, 68.83, 66.60, 65.57, 63.79, 63.37, 62.67, 62.45, 62.35, 60.49.

Linear 3,4-OEF-chloride: ^{1}H NMR (250 MHz, CDCl$_3$, δ): 7.93-8.05 (s, 2H, C$_{aromat}$H), 4.37-4.60 (m, 4H, CH$_2$ and 2H, CH$_2$-CH$_2$-Cl and 2H, CH$_2$-CH$_2$-O$_{ether}$), 3.72-3.86 (m, 2H, CH$_2$-Cl and

Table 1. Copolymerization of **cyc 3,4-OEF** using **PPDL** macroinitiators: reaction parameters and characterization data. Reactions were performed for 1 h at the temperature indicated. PDL = pentadecalactone repeat units, EF = ethylene furanoate repeat units. The number-average molar mass M_n and dispersity Đ were determined by GPC in chloroform using poly(methylmethacrylate) standards. The conversion and percentage of each repeat unit ([PDL]; [EF]$_{exp.}$ in the copolymer was calculated from the proton NMR integrals. Thermal properties were determined via DSC measurements. n.d.: glass temperature T_g not determined due to a very broad melting area overlapping the T_g range.

$M_{n,PPDL}$ [g mol⁻¹]	Đ	[PDL]:[EF]$_{calc.}$	$T_{react.}$ [°C]	Con-version [%]	$M_{n,product}$ [g mol⁻¹]	Đ$_{product}$	[PDL]:[EF]$_{exp}$	PDL block [%]	EF block [%]	T_g [°C]	T_m [°C]
2200	1.88	50:50	230	98	16 100	2.67	47:53	32	48	n.d.	10–50
			220	96	13 300	2.41	44:56	39	56	n.d.	10–50
			210	96	6800	2.06	48:52	47	58	n.d.	10–50
		80:20	230	≥99	10 500	2.25	81:19	69	17	—	72
			220	≥99	8800	2.09	84:16	74	19	—	73
			210	97	7700	2.02	80:20	82	34	—	77
8900	2.12	90:10	230	≥99	16 000	1.82	94:6	86	7	—	85
			220	≥99	15 700	1.84	95:5	90	0	—	86
			210	≥99	13 700	1.91	93:7	89	0	—	85

2H, CH_2-O$_{ether}$); ^{13}C NMR (63 MHz, CDCl₃, δ): 161.22, 161.01, 160.82, 149.48, 149.41, 149.29, 149.07, 117.82, 117.78, 117.64, 68.88, 64.36, 63.82, 62.45, 41.42.

2) Introduction of azide end groups. Oligomeric ethylene furanoate bearing chloride end groups (80.0 mg, 0.0421 mmol) was dissolved in DMF. NaN₃ (13.7 mg, 0.211 mmol) was added. The reaction mixture was allowed to stir for 4 days at room temperature. The solvent was removed by rotary evaporation. The crude product was dissolved in chloroform and NaCl. Unreacted NaN₃ was removed by filtration. The solvent was evaporated, and the product was dried under high vacuum yielding a beige solid (≈25% conversion of alkyl chloride end groups, 76% yield).

^{1}H NMR (250 MHz, CDCl₃, δ): 7.95-8.05 (s, 2H, C$_{aromat}H$), 4.38-4.60 (m, 4H, CH_2 and 2H, CH_2-CH₂-Cl and 2H, CH_2-CH₂-N₃ and 2H, CH_2-O$_{ether}$), 3.73-3.88 (m, 2H, CH_2-Cl and 2H, CH_2-O$_{ether}$), 3.56 (t, J = 4.9 Hz, CH_2-N₃); ^{13}C NMR (63 MHz, CDCl₃, δ): 163.45, 161.23, 161.03, 160.85, 151.84, 149.50, 149.43, 149.31, 149.08, 118.55, 117.82, 117.68, 68.91, 64.39, 63.82, 63.57, 62.48, 48.86, 41.44.

2.3.5. Synthesis of the Block Copolymer PPDL-triazole-OEF by Polymer-Analogous Reaction of End-Functionalized PPDL and OEF

The syntheses of poly(pentadecalactone) bearing an alkyne end group was described previously.[14] The data of PPDL end-functionalized with an azide group (PPDL-N3) used here can be found in that same paper.[14] In the glovebox, PPDL-alkyne (M_n = 6100 g mol⁻¹, Đ 2.45, 38.0 mg, 0.006 mmol PPDL chains), OEF-azide (M_n = 1900 kg mol⁻¹, Đ 1.17, 38.5 mg azide-functionalized OEF, 0.019 mmol azide-functionalized OEF chains), copper(I) acetate (Cu^{I}OAc) (0.764 mg, 0.006 mmol) and an equimolar amount of TBD (0.867 mg, 0.006 mmol) were placed in a Schlenk flask and dissolved in dry chloroform (5 mL). The reaction mixture was removed from the glovebox and stirred for 2 days at 40 °C. Afterward, the crude product was first precipitated into an excess of ethanol, then twice into an excess of *N,N*-dimethylformamide (DMF). The resulting polymer was dried in vacuum at room temperature for 2 days (M_n = 12400 g mol⁻¹, Đ 1.54).

^{1}H NMR (250 MHz, CDCl₃, δ): 7.91-8.08 (m, 2H$_{OEF}$, C = CH), 7.75-7.81 (m, 1H$_{triazole}$, H-C = C), 5.17-5.23 (m, 2H$_{PPDL}$, CH_2-C = C), 4.63-4.69 (m, 2H$_{OEF}$, CH_2-N), 4.45-4.61 (m, 4H$_{OEF}$, CH_2 and 2H$_{OEF}$, CH_2-CH₂-Cl and 2H$_{OEF}$, CH_2-CH₂-N), 4.38-4.45 (m, 2H$_{OEF}$, CH_2-CH₂-O$_{ether}$), 4.00-4.12 (m, 2H$_{PPDL}$, CH_2-O-C = O), 3.72-3.85 (m, 2H$_{OEF}$, CH_2-Cl and 2H, CH_2-O$_{ether}$), 3.62-3.68 (m, 2H$_{PPDL}$, CH_2-OH), 2.22-2.36 (m, 2H$_{PPDL}$, CH_2-C = O), 1.50-1.70 (m, 4H$_{PPDL}$, CH_2), 1.20-1.40 (m, 20H$_{PPDL}$, CH_2); ^{13}C NMR (63 MHz, CDCl₃, δ): 173.96, 161.01, 149.42, 117.80, 64.37, 62.46, 34.38, 29.60, 29.46, 29.25, 29.14, 28.64, 25.91, 25.00.

2.4. Film Formation from the Polymeric Material

Polymer films were formed via spin coating the respective polymer solution at a concentration of 20 mg mL⁻¹ onto different substrates. For PEF, pure silicon wafers were used; for the copolymer, more hydrophobic silicon wafers prefunctionalized with triethoxybenzophenone silane (3EBP-silane), were used. 3EBP-

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silane and the prefunctionalized wafers were prepared as described in previously.[15] The resulting polymer layers were placed onto a hot plate at 120 °C for 5 min to delete the processing history of the sample. Afterward, the samples were heated at 90 °C for 30 min and stored overnight at room temperature.
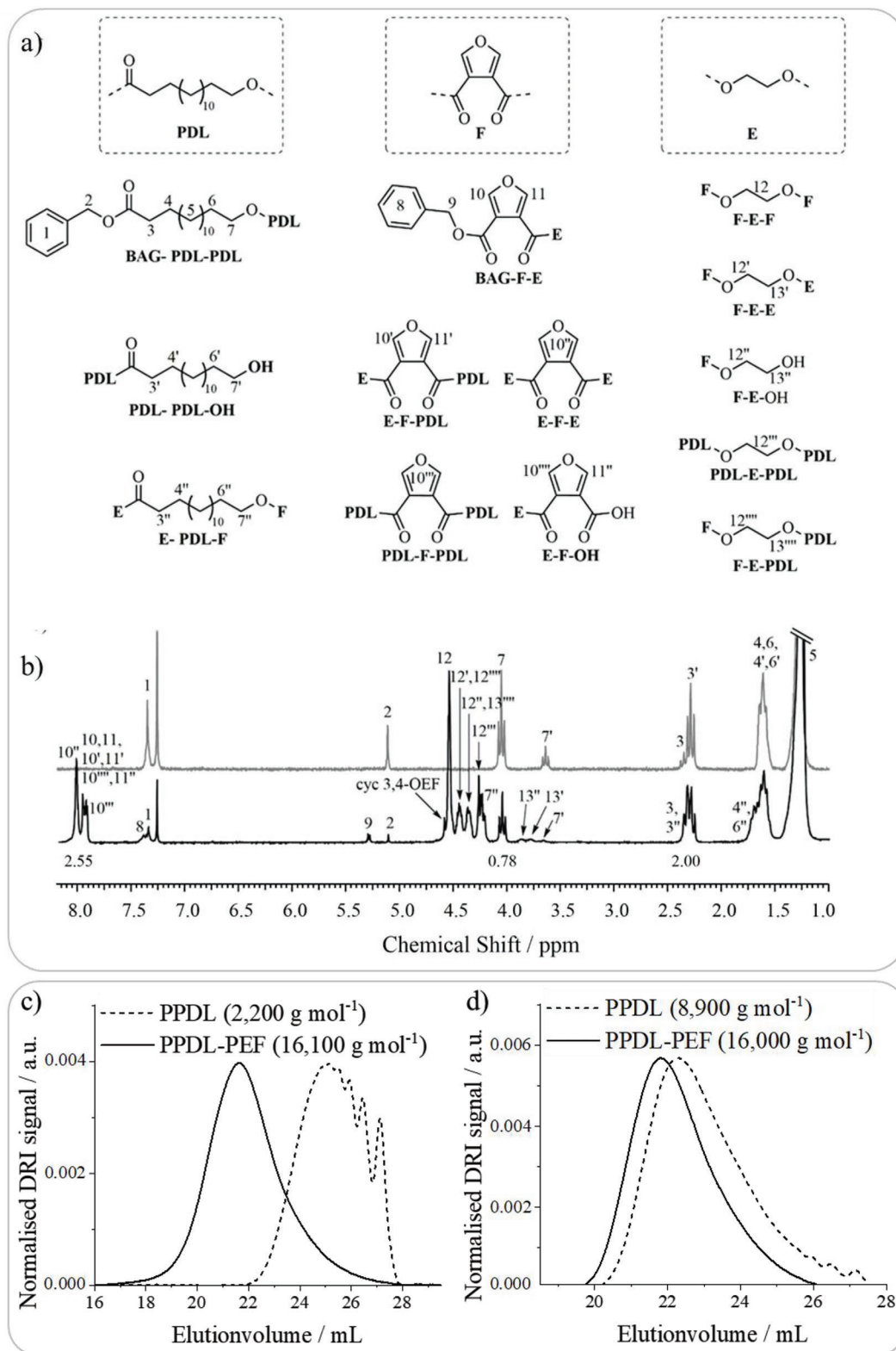
3. Results and Discussion

3.1. Macroinitiator Approach

With the aim of obtaining block copolymers of PEF and PPDL, first a macroinitiator approach was pursued, where a block of PPDL with an OH end group was used to try to initiate the polymerization of cyclic species of oligoethylene furanoate (**cyc 3,4-OEF**). **Cyc 3,4-OEF** was synthesized from dimethyl furan-3,4-dicarboxylate (**MeFDCA**), which was reacted with an excess of ethylene glycol in the presence of Bu_2SnO (Scheme 1a). After 5 h at 180 °C, **MeFDCA** was quantitatively converted into bis(2-hydroxyethyl) furan-3,4-dicarboxylate (**HEtFDCA**). This was confirmed by proton NMR measurements. ^{1}H-NMR spectra of **MeFDCA** and **HEtFDCA** can be found in Figure S1 in the Supporting Information. The singlet of **MeFDCA** at 7.95 ppm (for the protons of the furan ring) shifted to 8.06 ppm in **HEtFDCA**, and the singlet at 3.87 ppm, characteristic for the methyl groups of **MeFDCA**, vanished. New triplets at 4.41 and 3.89 ppm appeared, which are characteristic for the CH_2 groups of the attached ethylene glycol units. For the second reaction step (Scheme 1a), the high boiling point solvent dichlorobenzene (DCB) was added, so that the reaction mixture was highly diluted. These conditions favor the formation of **cyc 3,4-OEF** by self-condensation over the formation of the linear **3,4-OEF**. The reaction was stirred at 200 °C for 24 h, followed by removal of the formed alcohol and most of the solvent by distillation. The hot reaction mixture was then filtered to recover the precipitated linear **3,4-OEF**. **Cyc 3,4-OEF** partly precipitated while cooling down, and partly when the reaction mixture was added into cold pentane.

It was further purified by column chromatography. Proton NMR measurements of **cyc 3,4-OEF** showed a shift of the protons from the furan ring in **HEtFDCA** from 8.06 to 7.97 ppm in **cyc 3,4-OEF**. In addition, the two triplets from the ethylene glycol units vanished, and a large singlet at 4.60 ppm appeared (see Figure S1c, Supporting Information). The mass spectrum (ESI-MS) of the **cyc 3,4-OEF** fraction (Figure S2, Supporting Information) confirms that cyclic species formed, which had a ring size between two (m/z of 365.05 $[C_{16}H_{12}O_{10}H]^+$ and 387.03 $[C_{16}H_{12}O_{10}Na]^+$) and seven repeats units (m/z of 1297.13 $[C_{56}H_{42}O_{35}Na]^+$). The majority of the formed rings had three repeat units (m/z of 547.07 $[C_{24}H_{18}O_{15}H]^+$ and 569.05 $[C_{24}H_{18}O_{15}Na]^+$). The FTIR spectra of **cyc 3,4-OEF** is shown in Figure S3 (Supporting Information). The homopolymerization of **cyc 3,4-OEF** was studied as a model reaction for the planned initiation of **cyc 3,4-OEF** with poly(pentadecalactone) (**PPDL**). The melting range of the mixture of the **cyc 3,4-OEF** species obtained was from 200 to 215 °C, so that the melt polymerization of **cyc 3,4-OEF** (Scheme 1b) was performed above that temperature. To enable homogeneous mixing of the solid **cyc 3,4-OEF** and the polymerization catalyst tin octanoate ($Sn(Oct)_2$), both reactants were placed in a Schlenk tube and dissolved in DCM. After removing the solvent, the reaction was allowed to proceed at 230 °C

for 1 h. Proton NMR spectra of the product **3,4-PEF** revealed that by this time, all cyclic species were polymerized (Figure S4, Supporting Information). In these spectra, two singlets were present, one at 8.12 ppm for the protons of the furan ring and the other one at 4.67 ppm for the protons of the ethylene glycol part. No end group signals could be seen due to the high molar mass of the polymer. GPC measurements of **3,4-PEF** in hexafluoroisopropanol (HFIP) using PET standards gave a number-average molar mass of 60 000 g mol^{-1} and a dispersity of 1.68. The FTIR spectrum of **3,4-PEF** is included in Figure S3 in the Supporting Information. The thermal properties of **3,4-PEF** were studied by differential scanning calorimetry (DSC, Figure S5 in the Supporting Information). In the first heating curve, a melting temperature of 154 °C can be seen, but no recrystallization peak is found in the cooling curve. The second heating curve only shows the glass transition temperature at 40 °C. This phenomenon was also reported by Thiyagarajan et al.[1] and was explained by a very low rate of crystallization of that polymer. Since the polymerization of **cyc 3,4-OEF** was successful under these conditions, the same reaction parameters were applied in the attempts to initiate the polymerization of **cyc 3,4-OEF** with **PPDL** as a macroinitiator (Scheme 1c). The synthesis of the **PPDL** initiator with an OH end group has been reported in two previous papers.[9,10] When **PPDL** alone was subject to the chosen reaction conditions, it was stable, as no structural changes were observed in ^{1}H-NMR and GPC measurements. For the attempted block copolymer syntheses, two **PPDL** macroinitiators with different molar masses (2200 and 8900 g mol^{-1}, respectively) were chosen. With these, reactions with three different molar ratios of pentadecalactone to ethylene furanote repeat units (50:50, 80:20, and 90:10), and three different reaction temperatures (210, 220, and 230 °C) were performed, as summarized in Table 1.

In all reactions, **PPDL**, **cyc 3,4-OEF**, and $Sn(Oct)_2$ were placed in a Schlenk tube, homogenized by dissolution in DCM, and dried under high vacuum. The reaction mixture was then kept at the designated temperature for 1 h, as described for the synthesis of the **3,4-PEF** homopolymer. Instead of the desired block copolymers, copolymers with both a statistical and a blocky distribution of PPDL and OEF units were obtained, as revealed by ^{1}H-NMR spectroscopy. This was a result of transesterification throughout the polymer. In the NMR spectra, three main repeat units of the **PPDL-PEF** copolymer were identified: ethyleneoxy (**E**), furanoate (**F**), and pentadecalactone (**PDL**, **Figure 1a**). Figure 1b presents an overlay of the proton NMR spectrum of the **PPDL-PEF** copolymer with a M_n of 13 300 g mol^{-1} (line 2 in Table 1, black line in Figure 1b) and the **PPDL** macroinitiator with a M_n of 2200 g mol^{-1} (gray line in Figure 1b). In the spectrum of the copolymer, all signals from the macroinitiator are still visible, meaning that PPDL in a blocky environment is still present, but the intensities as well as the shapes of these signals are changed due to transesterification within the **PPDL** chains. The signals corresponding to the transesterification products indicated in Figure 1a were assigned in the copolymer spectrum in Figure 1b. In addition, different end group signals were visible, e.g., the signals of the CH_2 groups next to a hydroxyl group at around 3.65 ppm for the PPDL chains, and around 3.87 ppm for the PEF chains. Furthermore, end group signals of the former benzyl alcohol initiator that was used for the synthesis of the **PPDL** macroinitiator are visible at 5.11 and 7.35 ppm. Due to transesterification with

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Figure 1. a) Chemical structures of the end group from the initiator benzyl alcohol (**BAG**) as well as the repeat units found in the polyester **PPDL-PEF**: pentadecalactone (**PDL**), furanoate (**F**), and ethyleneoxy (**E**). b) ^{1}H-NMR spectra of the **PPDL** macro-initiator (M_n = 2200 g mol^{-1}) and the resulting copolymer **PPDL-PEF** (M_n = 13 300 g mol^{-1}, all in CDCl$_3$ at 250 MHz); c) GPC curves of two **PPDL-PEF** copolymers with M_n = 16 100 g mol^{-1} and M_n = 16 000 g mol^{-1} (black line) and the corresponding **PPDL** macroinitiators (dashed line).

furanoate species, new signals like the singlet at 5.29 ppm and the multiplet at around 7.38 ppm appeared. In the aromatic region, a singlet at 8.02 ppm (characteristic for aromatic CH groups in a PEF chain) and a singlet at 7.93 ppm (aromatic CH group of furanoate structure between two PDL species) were found. If different chemical species are attached to each side of a furane ring, two signals instead of one appear for symmetry reasons. Such signals were found at 7.95 ppm.

Between 4.20 and 4.60 ppm, different signals corresponding to O-CH$_2$ groups of the ethyleneoxy and PDL units were found: a singlet at 4.55 ppm (ethyleneoxy group between two furanoate species), a singlet at 4.27 ppm (ethyleneoxy group between two PDL species), and a smaller signal at 4.59 ppm, which corresponds to the unreacted cyclic species. The multiplet around 4.45 ppm contained signals of F-O-CH_2-CH$_2$-O-PDL and of CH_2-CH$_2$-O$_{ether}$. The multiplet at 4.36 ppm had signals from CH_2-CH$_2$-OH and from F-O-CH$_2$-CH_2-O-PDL. The signals at around 4.23 ppm were assigned to the O-CH$_2$ of the PDL chain next to a furanoate species. The formation of this new species goes along with a decrease in the integral intensity of the triplet at 4.05 ppm which was assigned to the O-CH$_2$ of **PPDL**. The signal at 3.78 ppm was assigned to the O-CH$_2$ ether group of two neighboring ethyleneoxy groups. In the area between 2.24 and 2.41 ppm, signals of CH_2-C=O from the PDL structure were located. The shape change of this signal from the copolymer in comparison to the one from the **PPDL** initiator is evidence that there was transesterification within the former **PPDL** block. Not only benzyl alcohol and PDL units were found next to CH$_2$-C=O groups, but also ethyleneoxy groups, which is also the result of transesterification within the **PPDL** block. Furthermore, the signal at 1.61 ppm broadened due to the presence of PDL between ethyleneoxy and furanoate species. As the **PPDL** macroinitiator by itself did not undergo structural or molar mass changes under the same reaction conditions, it can be safely assumed that the transesterification was induced by reactions of **PPDL** with the cyclic oligomers of ethylene furanoate.

In all reactions studied, an increase in the molar mass of the product compared to the macroinitiator was observed. Examples of GPC curves of **PPDL-PEF** copolymers (M_n = 16 000 g mol^{-1}) and their corresponding **PPDL** macroinitiators (with molar masses of 2200 and 8900 g mol^{-1}, respectively) are shown in Figure 1c. Both copolymers had monomodal GPC curves with the peak maximum shifted toward lower elution volumes compared to the macroinitiators. Additionally, the curves of the copolymer did not show the oligomeric signals found in the macroinitiator elugrams from 26 to 28 mL. This proves that those chains must have reacted. In the three reaction sets with different ratios of PDL to OEF repeat units (90:10, 80:20, and 50:50, respectively), the molar masses of the obtained copolymers increased most when a reaction temperature of 230 °C was chosen. For example, the reaction at a 50:50 ratio (line 1 in Table 1) gave a molar mass of 16 100 g mol^{-1} at 230 °C, but the molar mass reached only 6800 g mol^{-1} at 210 °C. Higher reaction temperatures also favor the transesterification process, so that less PDL and EF block structures were found by proton NMR. The amount of PDL in a blocky environment was calculated from these spectra using the integral of the triplet at 3.05 ppm (PDL next to another PDL unit and therefore characteristic for the PDL block). This data were then related to the integral of the signals at 2.3 ppm, since

this integral in the PPDL homopolymer should have the same intensity as the signals at 3.05 ppm. To determine the amount of blocky PEF in the reaction product, the ratio of the singlet at 8.02 ppm (protons from a furan ring next to an ethyleneoxy unit) was related to the other aromatic signals around 8 ppm. Thus, the above-mentioned reaction product obtained at 210 °C had 47% PDL block structure and 58% ethylene furanoates (EF) block structure. For the same reaction conducted at 230 °C, the amount of PDL in a blocky environment was only 32% and that of EF block only 48%.
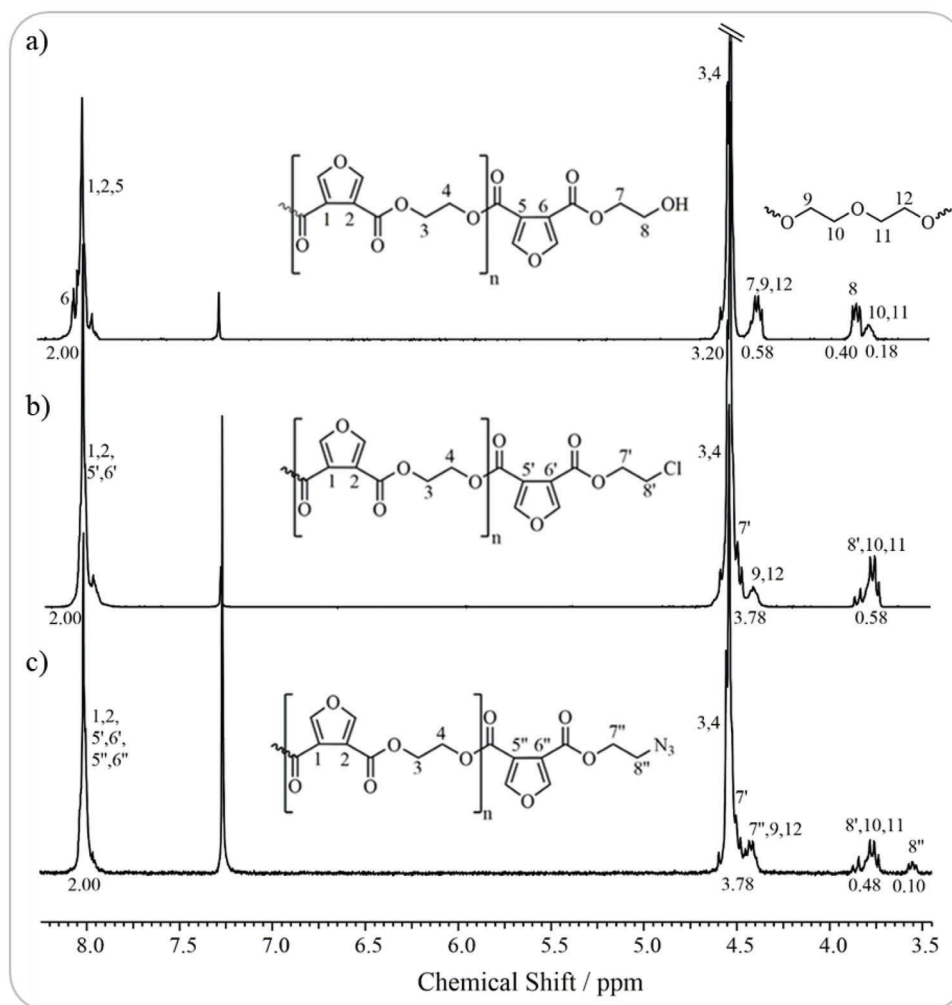
The ratio of the initial PDL units of the **PPDL** macroinitiator and the EF units of **cyc 3,4-OEF** also influenced the blockiness of the resulting copolymers. If the PDL content was 90%, all **cyc 3,4-OEF** was polymerized, and no or only very little amounts of EF blocks were found, so that overall, the transesterification reaction dominated. When the reactions were conducted at a ratio of 80:20, **cyc 3,4-OEF** was polymerized, and the EF block content was between 17% and 34%. If the ratio was 50:50, between 96% and 98% of **cyc 3,4-OEF** were polymerized, and the EF block content was between 48% and 58%. Thus, with increasing amounts of **cyc 3,4-OEF**, the amount of EF blocks in the copolymer increased.

Expectedly, the ratio of the repeat units and its impact on the blockiness strongly affected the thermal properties of the copolymers obtained. The results of the DSC measurements can be found in Figure S6 (Supporting Information). Copolymers with a repeat unit ratio of 50:50 had a broad melting area (between 10 and 50 °C, see Figure S6a, Supporting Information), which overlapped with the range where the glass transition temperature was expected. The 80:20 copolymer (Figure S6b, Supporting Information) did not show a distinct glass transition temperature in the expected range, but a clear melting peak at 72 °C. The DSC curves of copolymers with a ratio of 90:10 also only showed a sharp melting point at 85 °C (see Figure S6c, Supporting Information), which is slightly lower than the value obtained for PPDL homopolymers. Thus, the melting temperature of the PPDL part of each copolymer shifts to higher temperatures with increasing PDL repeat unit ratios and increasing blockiness of the copolymers. The broad melting area of the 50:50 sample with different peak maxima thus confirms the high degree of transesterification of that copolymer.

3.2. "Click" Approach

Since the above described macroinitiator approach gave copolymers with undesired transesterification throughout the polymer chains, homopolymers of **PPDL** and **3,4-PEF** were functionalized with reactive end groups and connected under reaction conditions that do not induce transesterification. The copper-catalyzed 1,3-dipolar addition ("click reaction") between one block carrying an azide group and the other block carrying an alkyne group (Scheme 1d,e) is such a reaction. The functionalization of the **3,4-PEF** homopolymer with a reactive end group proved difficult because the PEF homopolymer has a poor solubility—it only dissolves in hexafluoroisopropanol (HFIP) and trifluoroacetic acid (TFA). Both are protic solvents and therefore not suitable for the intended functionalization by nucleophilic substitution. Thus, instead of high molar mass **3,4-PEF**, the linear ethylene

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Figure 2. ^{1}H-NMR spectra of a) linear **3,4-OEF**, b) linear **3,4-OEF-chloride,** and c) linear **3,4-OEF-azide** (all in CDCl3 at 250 MHz).

furanoate oligomers (**3,4-OEF**, molar mass around 2000 g mol^{-1}) that formed as byproducts in the synthesis of **cyc 3,4-OEF** were used as model compounds. These were soluble in common solvents like DCM or chloroform. Characterization details of the linear **3,4-OEFs** are found in the FTIR spectrum (Figure S7, Supporting Information) and in **Figure 2a**.

Their proton NMR spectrum featured signals around 8.00 ppm which are characteristic for protons of the furan ring. The strong singlet at 4.54 ppm resulted from protons in the middle of the OEF chain. At lower ppm values, signals from CH$_2$-O-C=O groups next to the hydroxyl end groups of the polymer as well as ether groups were found. The triplet at 3.85 ppm was assigned to CH$_2$ groups next to a hydroxyl end group and the signal at 3.78 ppm to a CH group next to an ether group between two ethyleneoxy groups.

The thus identified free hydroxyl end groups in **3,4-OEF** were used to introduce an azide end group by nucleophilic substitution. Since hydroxyl groups are poor leaving groups in nucleophilic substitution reactions, they were first converted into more reactive chloride groups using thionyl chloride. Those could be transformed into azide end groups in another nucleophilic sub-

stitution reaction with sodium azide (Scheme 1d). In the first step, linear **3,4-OEF** (number-average molar mass: 1900 g mol^{-1}) dissolved in chloroform was refluxed with thionyl chloride and catalytic amounts of *N,N*-dimethyl formamide (DMF) for 4 days. The proton NMR spectrum (Figure 2b) indicated full conversion of the hydroxyl end groups into the corresponding chloride, since the NMR signal of the CH$_2$ group next to the hydroxyl end group at 3.85 ppm vanished, and a new signal corresponding to the CH$_2$-Cl group appeared at around 3.74 ppm, in addition to a signal originating from the CH_2-CH$_2$-Cl group at 4.50 ppm. Also, the signals in the aromatic region changed. The singlet at 8.06 ppm assigned to the CH group of the furan ring next to the hydroxyl end group vanished. The FTIR spectrum of **3,4-OEF chloride** (Figure S7, Supporting Information) showed the expected new signal at 667 cm^{-1}, characteristic for alkyl halides. In addition, the broad signal at 3400 cm^{-1} vanished, which further proves the removal of free hydroxyl end groups. A shoulder of the carbonyl band (at 1795 cm^{-1}) indicated the formation of an acid chloride groups and thereby suggests that in addition to the OH end groups, free acid end groups must have been present in the **3,4-OEF** starting material. For the second step,

the azide functionalization, **3,4-OEF chloride** was dissolved in DMF, and NaN$_3$ was added. The reaction mixture was stirred for 4 days at room temperature. The NMR spectrum of the reaction product (Figure 2c) indicates that unreacted chloride remained in the reaction mixture. However, a new triplet at 3.56 ppm which is characteristic for CH$_2$ groups next to an azide group appeared, indicating that a partial functionalization was obtained. The conversion from chloride to azide was determined by integration and amounted to 25%. The results of the FTIR characterization (Figure S7, Supporting Information) support this interpretation.

For a better understanding of the end group situation in the linear **3,4-OEFs** and their derivatives, matrix-assisted, laser desorption and ionization, time-of-flight mass spectra (MALDI-TOF MS) were recorded (**Figure 3**). The structures of the here described oligomeric species **3,4-OEF**, **3,4-OEF chloride,** and **3,4-OEF azide** are shown in Figure 3a. In Figure 3b, the entire MALDI-TOF MS of the linear **3,4-OEF** is shown, together with a magnified section from that spectrum (Figure 3c) and from the spectra of **3,4-OEF chloride** (Figure 3d) and **3,4-OEF azide** (Figure 3e). Figure 3b indicates that oligomers with six repeat units were the most abundant species, and oligomers with up to 11 repeat units were found. The magnified section of the spectrum with multiple other distributions around the most intense signals (Figure 3c) showed that the end group situation was already highly heterogeneous in linear **3,4-OEF** before the first functionalization step. Possible end-group structures are assigned to the peaks in Figure 3c. All signals could be assigned, but some structures theoretically had the same masses and thus could not be distinguished. Therefore, it was not possible to quantify the ratio of end groups present. In Figure 3d, all signals could be assigned to oligomeric species bearing chloride end groups on both sides of the chain, no matter whether they were acid chloride or alkyl chloride groups. Further structures are indicated in the same figure. In Figure 3e, the MALDI-TOF spectrum of **3,4-OEF-azide** is shown. As only partial functionalization was found by NMR, it is not surprising that this spectrum strongly resembles the **3,4-OEF-chloride** spectrum, except for a few smaller new signals.

Also, some new signals of species with azide end groups could be overlapping with the signals from the **3,4-OEF-chloride** starting material, so that a specific assignment and quantification was not always possible. The probable new signals of **3,4-OEF-azide** species were included Figure 3e in gray color. In summary, the analytics indicate that the functionalization with azide was only partial. Not all the end groups of **3,4-OEF-chloride** had the desired alkyl chloride end groups, and the conversion of **3,4-OEF-chloride** with the "correct" alkyl chloride end groups to the azide group was limited.
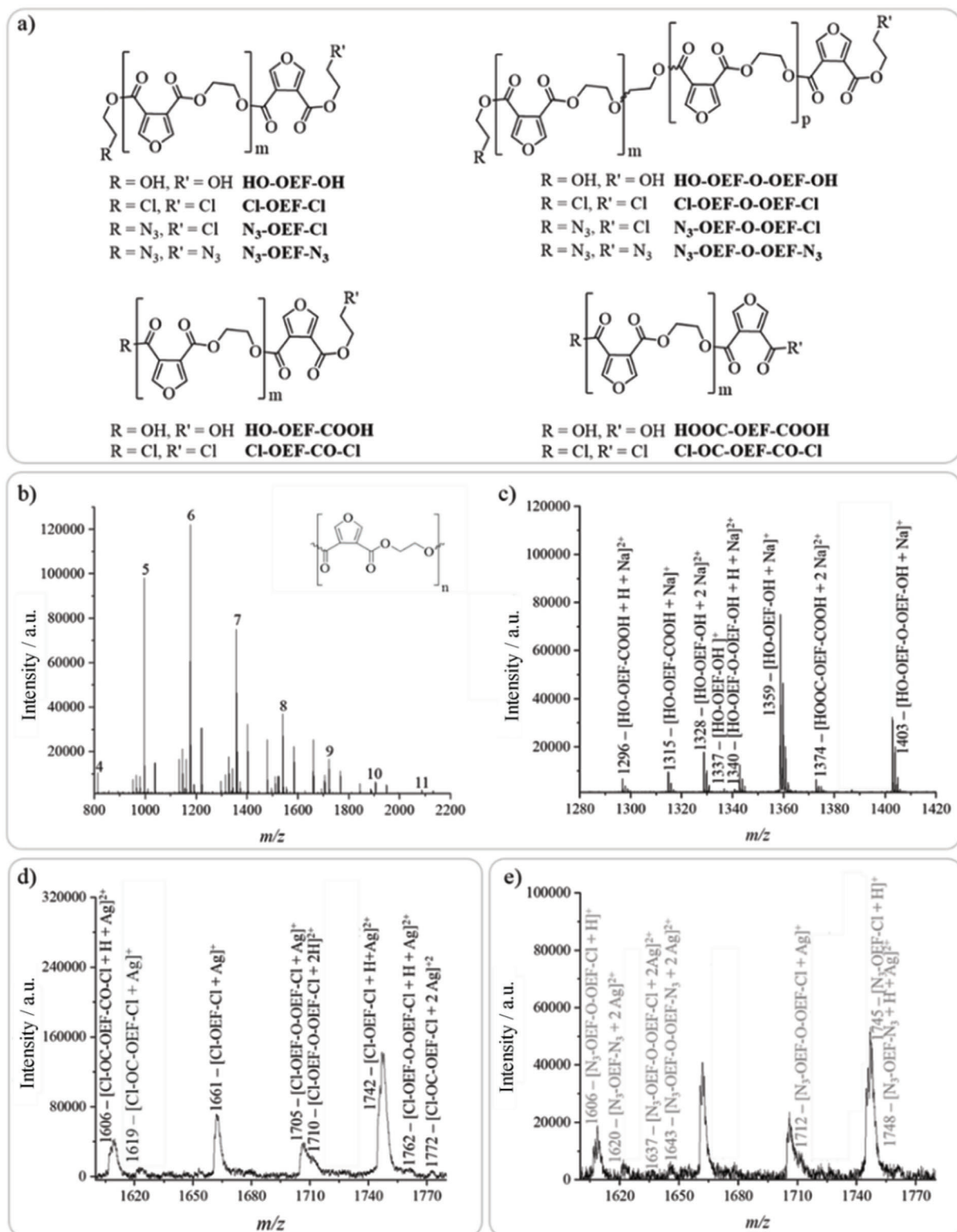
Since the **3,4-OEF-azide** oligomers were only partly functionalized with azide end groups, an excess of **3,4-OEF-azide** was used for the copper catalysed azide-alkyne cycloaddition reaction between **3,4-OEF-azide** and **PPDL-alkyne**. The synthesis of **PPDL-alkyne** was reported in a previous paper.[10] In order to link **3,4-OEF-azide** (M_n = 1900 g mol^{-1}, Đ 1.17) and **PPDL-alkyne** (M_n = 6100 g mol^{-1}, Đ = 2.45, Scheme 1a), they were stirred with Cu^{I}OAc and triazabicyclodecene in chloroform for 2 days at 40 °C. The crude product was then precipitated into an ex-

cess of ethanol to remove the catalyst, and twice into an excess of *N,N*-dimethylformamide (DMF) to remove the excess of **3,4-OEF-azide**. This step also removed any oligomeric ethylene furanoate species that were not azide functionalized, since they were all soluble in DMF, while the formed **PPDL-triazole-OEF** block copolymer **PPDL** was not.
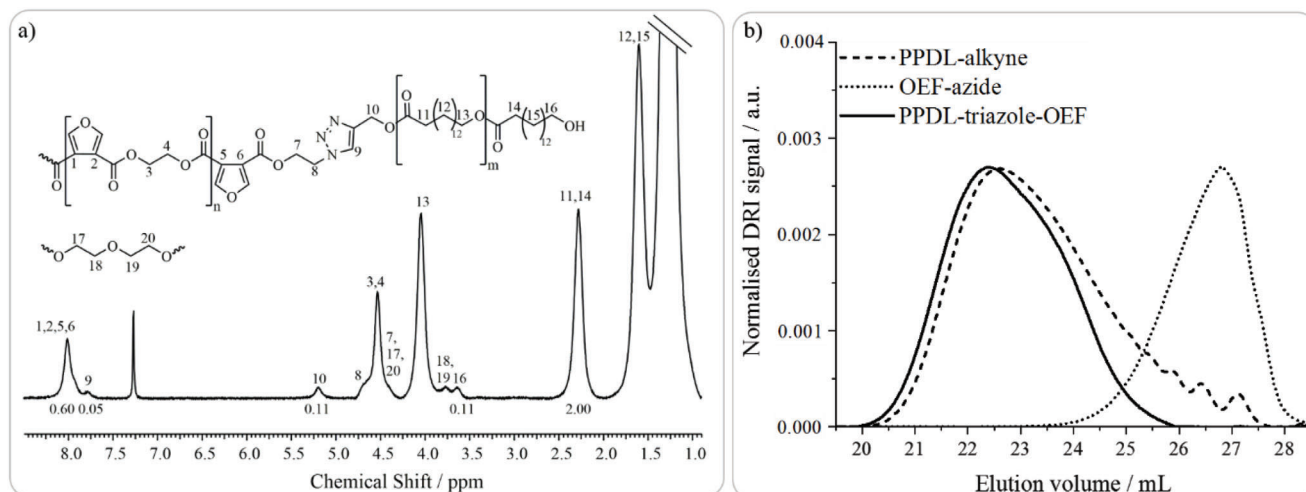
The proton NMR spectrum of **PPDL-triazole-OEF** is shown in **Figure 4a**. All characteristic signals from **3,4-OEF** and **PPDL** are present: the signals of the protons from the furan ring are located at around 8 ppm, and the ones from the CH$_2$ groups of ethylene at 4.6 ppm. The signal of the former CH$_2$ group next to the azide at 3.56 ppm vanished, which proves that those end groups must have reacted. A new signal of this CH$_2$ group next to the triazole ring is found at 4.66 ppm. Signals at 7.78 and 5.20 ppm, which could be assigned to the CH group of the triazole ring and the CH$_2$ group of PPDL next to it, are another proof for the successful triazole formation. Furthermore, no proton signals of the former alkyne group (e.g., the signal at 2.47 ppm) could be found, indicating that all alkyne groups must have reacted. From the ratio of the C(=O)-CH_2 signal of the PPDL block and the aromatic signals from the OEF block, a OEF amount of 23% and a PPDL amount of 77% was calculated.

Figure 4b shows the GPC curves of the block copolymer **PPDL-triazole-OEF** and the functionalized homopolymers **PPDL-alkyne** and **3,4-OEF-azide**. The number-average molar mass of the block copolymer was 12 400 g mol^{-1}, with a dispersity of 1.54. The curve of the copolymer showed a shift of the peak maximum toward lower elution volumes, indicating an increase in molar mass. The peaks of the homopolymer elugrams in the area between 26 and 28 mL, where the oligomeric species could be found before, had vanished in the copolymer elugram. This proves that those chains must have reacted by increasing their molar masses.

The MALDI-TOF MS measurements of **3,4-OEF-azide** had revealed that oligomeric chains with one or two azide end groups were synthesized. Therefore, it is possible that triblock copolymers formed as a side product besides the target block copolymers. This possibility could be neither proven nor disproven based on these GPC elugrams. The FTIR spectrum of **PPDL-triazole-OEF** is shown in Figure S8 in the Supporting Information. Characteristic signals of both polymer species were found (strong ester bond at 1722 cm^{-1}, signals at 1541 and 1577 cm^{-1} characteristic for the aromatic species). This indicates that both homopolymers were incorporated into the copolymer. The homopolymer signals of the azide group at 2102 cm^{-1} and of the alkyne group at 3307 cm^{-1} vanished. The newly formed triazole signals (1636 and 1463 cm^{-1}, belonging to C=C and C—H vibrations) overlapped with signals from the homopolymers and therefore were not clearly identified. Figure S9 in the Supporting Information shows the DSC curve of the **PPDL-triazole-OEF** block copolymer. A sharp melting peak at 90 °C was found in the heating curve, as well as a recrystallization temperature of 78 °C. Both originate from the PPDL block. No distinct glass transition temperature of the OEF block could be observed in the heating curve. This is not surprising since there were only 23% OEF repeat units in that copolymer. These results are consistent with the previously assumed block copolymer nature of these compounds.

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Figure 3. a) Structures of the here described oligomeric species **3,4-OEF**, **3,4-OEF chloride,** and **3,4-OEF azide**. MALDI-TOF spectrum of **3,4-OEF** and its derivatives: b) full **3,4-OEF** spectrum, c) close-up of the region between m/z from 1280 to 1420 in **3,4-OEF**. For d) **3,4-OEF-chloride** and e) **3,4-OEF-azide**. Silver was used for ionization. For these oligomers, a close-up of the region between m/z from 1600 to 1780 is shown. Since the spectrum of **3,4-OEF-azide** showed almost the same signals like the spectrum of **3,4-OEF-chloride**, only the possible new azide-functionalized species signals are shown in gray, while the ones from the former chloride species are omitted. *trans*-2-[3-(4-tert-butylphenyl)−2-methyl-2-propenyliden]malononitrile (DCTB) was used as ionization matrix, together with sodium counterions unless indicated otherwise.

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Figure 4. a) ^{1}H-NMR spectrum of the block copolymer **PPDL-triazole-OEF** (M_n = 12 400 g mol^{-1}, $Đ$ = 1.54) in CDCl$_3$ at 250 MHz. b) GPC curves of **PPDL-triazole-OEF** (black line) and the end-functionalized homopolymers **PPDL-alkyne** (M_n = 6100 g mol^{-1}, $Đ$ 2.45) (dashed line) and **3,4-OEF-azide** (M_n = 1900 g mol^{-1}, $Đ$ 1.17) (dotted line).

3.3. Film Formation Studies

Thin films of **PPDL-triazole-OEF** were cast onto silicon wafers and investigated by atomic force microscopy (AFM) to study the morphology of the block copolymer in comparison to the homopolymers. A homopolymer blend could not be cast as a reference as no common solvent of PPDL and **3,4-PEF** was found. **PEF** was coated from HFIP onto plain silicon wafers. **PPDL** and the block copolymer were spin-cast for a chloroform solution onto silicon wafers which were prefunctionalized with a hydrophobic silane, as that wafer surface was a better match with the hydrophobicity of these polymers. Afterward, the polymer layers were heated on a hot plate at 120 °C for 5 min to delete their processing history, followed by heating at 90 °C for 30 min. The were then stored overnight at room temperature. The films were studied with different methods (Table 2). Films made from the block copolymer **PPDL-triazole-OEF** and the **PPDL** homopolymer, with a film thickness of around 100 nm, were hydrophobic (static contact angles around 93°, advancing and receding contact angels of 79° and 60°, respectively). The more hydrophilic **3,4-PEF** films with a thickness of around 74 nm had the expected lower contact angles (Table 2).

AFM height pictures of the block copolymer as well as the aromatic homopolymer are shown in **Figure 5**. The respective in phase and quadrature pictures are shown in the Supporting Information in Figure S10, together with the previously published **PPDL** images. **PPDL-triazole-OEF** (Figure 5a) showed spherulite

structures, which was also be found for **PPDL**. For the block copolymers, the diameters of the spherulites were smaller (average length: 33 μm; average width: 23 μm) than for the **PPDL** homopolymer (diameter > 250 μm). In addition, small vacancies were observed between the spherulite lamellae of the copolymer layer. Those were up to 37 nm deep and 250 nm wide. The overall roughness of the block copolymer layer was 4.9 nm. This is lower than the overall roughness of the **PPDL** layer with 8.6 nm, but higher than for the **3,4-PEF** surface. **3,4-PEF** normally is a semicrystalline polymer. Under the conditions used here, the **3,4-PEF** film (Figure 5b) was amorphous, with a very low roughness of 0.3 nm. Due to the high amount of **PPDL** in the block copolymer, it is not surprising that the structure of the copolymer film resembles the one of **PPDL**. A direct comparison and a more detailed discussion is difficult due to the differences in molar mass of the **PPDL** reference sample and the mass of the **PPDL** macroinitiator used.

To further analyze the copolymer film, quantitative nanomechanical AFM studies (QNM-AMF) were performed (Figures S11 and S12, Supporting Information). The elastic modulus of the samples was calculated using the Derjaguin–Muller–Toporov (DMT) model. **3,4-PEF** had a DMT modulus of 61.5 ± 5.4 MPa and was thus softer than **PPDL** with a DMT modulus of 801 ± 42 MPa.[10] The block copolymer **PPDL-triazole-OEF** had an intermediate DMT modulus of 647 ± 35 MPa, which is more in the range of the **PPDL** homopolymer value due to the higher amount of the aliphatic block.

Table 2. Thickness and contact angles (CA) of polymer films made from **PPDL**, **3,4-PEF**, and the block copolymer **PPDL-triazole-OEF**. The thickness was determined by ellipsometry.

	M_n [g mol^{-1}]	Static CA [°]	Advancing CA [°]	Receding CA [°]	Thickness[nm]
PPDL	32 000	93 ± 2	96 ± 2	61 ± 3	97 ± 2
3,4-PEF	60 000	36 ± 2	49 ± 2	22 ± 4	74 ± 5
PPDL-triazole-OEF	12 400	92 ± 2	98 ± 2	59 ± 3	99 ± 2
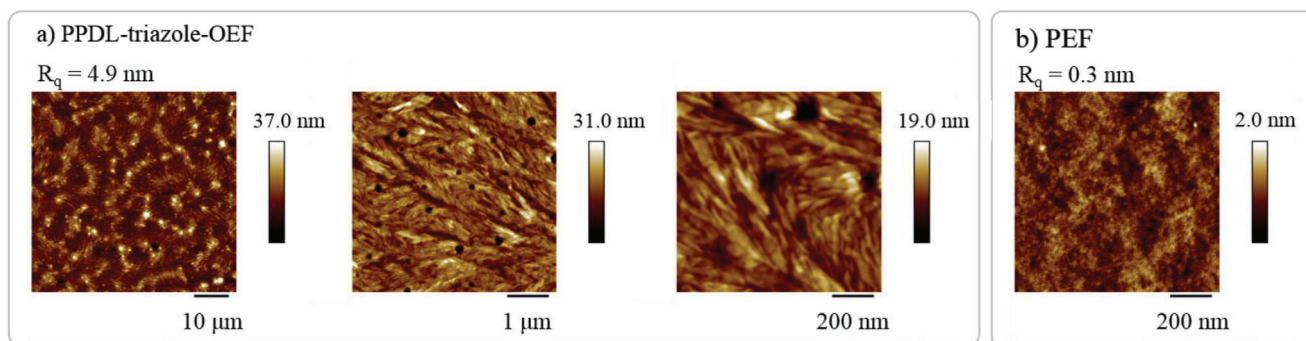
Figure 5. AFM height images and roughness data of films made from a) **PPDL-triazole-OEF** (M_n = 12 400 g mol^{-1}) and b) **PEF** homopolymer (M_n = 60 000 g mol^{-1}).

4. Discussion

The field of PPDL synthesis has made significant progress and a number novel of polymerization catalysts have been reported.[16–18] In consequence, all-degradable block copolymers with a PPDL block and another aliphatic block have been reported. Pepels and coworkers used aluminum complexes as catalysts and reported block copolymers with poly(lactic acid) with high dispersity due to intra-block transesterification but no inter-block transesterification.[19] With organic catalysts, the block copolymer dispersity of this system remained low, indicating that transesterification was not present.[20] In one-pot copolymerization reactions of menthide and PDL, block-like structures were obtained, again with intra-block transesterification but no intra-block transesterification.[21] In contrast, one-pot copolymerization reactions with lactones of ring sizes 6, 7, 9, and 13 atoms gave statistical copolymers.[21] In such one-pot reactions, smaller lactones are generally consumed before PDL due to their higher ring strain, so that block copolymers could be obtained from such systems unless transesterification leads to a statistical distribution.[7] Such transesterification can also be suppressed when using Lewis acids as cocatalysts.[22] Also, in sequential copolymerizations with cyclic trimeric phosphazene bases, the PPDL that was prepared first was able to initiate the polymerization of the small lactones, so that block copolymers were obtained.[23] The field of all-degradable aliphatic-aromatic block copolymers containing PPDL remains scarcely populated. This is due to a lack of suitable aromatic building blocks. In previous work, we had reported the synthesis of block copolymers of PPDL with dihydro-5H-1,4-benzodioxepin-5-one.[10] In a sequential approach, PPDL was used to initiate the second block. No transesterification was observed. However, the molar mass of the second block remained limited, so that a click-approach like the one presented here was developed. This lead to block copolymers with molar masses between 30 000 and 50 000 g mol^{-1}.[10] In another approach, we end-functionalized aromatic poly(3-hydroxycinnamate) obtained by polycondensation with azide groups and reacted the aromatic polymer with alkyne-functionalized PPDL.[9] Again, the molar mass of the aromatic block was limited. In the light of these results, in the present work, it was attempted to overcome the shortcomings of these reactions, and to obtain the desired block copolymers in sequential ring-opening polymerizations of **PDL** and **cyc 3,4-OEF**. Unfortunately, the copolymers obtained underwent transesterification, and the obtained molar masses also remained low (< 20 000 g mol^{-1}). Again, the synthetically more elaborate click approach had to be pursued to obtain the desired block copolymers. In comparison to the block copolymers of PPDL with dihydro-5H-1,4-benzodioxepin-5-one, which were obtained at only 40 °C,[10] it is clear that the high reaction temperatures of 210–230 °C for the **PDL** and **cyc 3,4-OEF** system are responsible for the undesired transesterification, but lower temperatures could not be applied due to the high melting point of the **cyc 3,4-OEF** oligomers. Also, unlike the copolymerization of **PDL** and the aliphatic lactones mentioned above (which were much more reactive due to their higher ring strain), the ring strain differences of **PDL** and **cyc 3,4-OEF** are too small to be exploited for a fast, preferential polymerization of one monomer in a sequential approach, which would avoid transesterification during long reaction times. In consequence, the click approach is—so far—the only viable avenue to block copolymers of this systems. Other suitable bio-based, degradable aromatic blocks need to be found to investigate the field of all-degradable aliphatic-aromatic block copolymers further. Very recently, salicylate aldehyde-based 7-membered lactone rings with aromatic substituents have been reported, which were also polymerizable by ring-opening polymerization.[24] With the high molar masses obtained for this system, they are promising candidates for block copolymer synthesis with PPDL.

5. Conclusion

We here presented the synthesis of block copolymers of poly(pentadecalactone) and poly(ethylen-3,4-furane dicarboxylate). In a sequential approach using the PPDL block as a macroinitiator for the ring-opening polymerization of oligo(ethylene-3,4-furandicarboxylate), only copolymers with varying amounts of blocky sequences were obtained, with the blockiness depending on the ratio of the PDL to PEF repeat units and the reaction temperature. When polymerizing each monomer separately and end-functionalizing the obtained polymer chains, they could be connected in a cooper-catalyzed 1,3-dipolar cycloaddition reaction ("click-reaction"). However, due to the poor solubility of poly(ethylen-3,4-furane dicarboxylate) at high molar masses, this approach yielded block copolymers with molar masses < 20 000 g mol^{-1}. While these molecules are academically interesting, their synthesis is too

elaborate for realistic applications as phase compatibilizers. The strong polarity difference of the two blocks, which has been seen when studying their surface properties, makes this system unique compared to the PPDL block copolymers previously studied by us. Such amphiphilic structures should be studied in more detail in future work.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords

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