

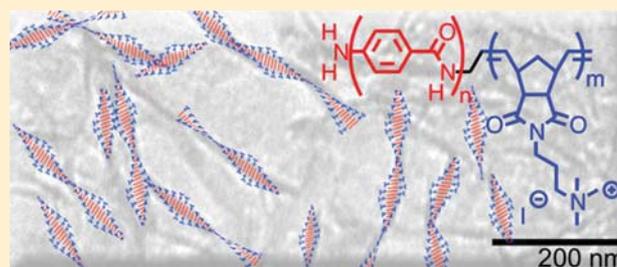
Facile Synthesis of a High Molecular Weight Amphiphilic Aramid–ROMP Block Copolymer

Michael Badoux, Susanne Drechsler, Subhajit Pal, and Andreas F. M. Kilbinger*[✉]

Chemistry Department, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland

S Supporting Information

ABSTRACT: Herein we report the facile synthesis of an amphiphilic rod–coil block copolymer obtained by the coupling of an amine-terminated poly(dimethylpropylamine norbornene imide) (PDMAPNI) and a pentafluorophenol ester-terminated poly(dimethoxybenzyl *p*-aminobenzoate) (PArAm). Postpolymerization amide N-deprotection of the block copolymer yielded a strongly aggregating water-soluble rod–coil copolymer. Transmission electron microscopy revealed the formation of large ribbonlike aggregates with sizes up to 50 nm in thickness and 300 nm in length.



INTRODUCTION

Over the past decades, many efforts have been directed toward the synthesis of well-defined block copolymers due to their unique and tunable properties compared to homopolymers. A diverse number of the reported polymers show the ability to self-assemble in solution, most often as a consequence of solvophobic effects.^{1,2} The range of structures that can be adopted by block copolymers varies from vesicles^{3,4} or micelles^{5–7} to nanotubes^{8–10} depending on parameters such as the nature of the different blocks or their length, for example. Block copolymer self-assemblies open the door to nanostructured materials possessing intriguing properties and have already shown to be useful for applications in optical devices,¹¹ advanced lithography,¹² drug release,¹³ or microelectronics.¹⁴

Ring-opening metathesis polymerization (ROMP) is an ideal choice when it comes to the synthesis of functional polymers. On the one hand, this method tolerates a large number of functional groups and is therefore suitable to prepare functional polymer blocks¹⁵ derived from functional monomers. On the other hand, its living polymerization character enables the direct attachment of a further block via ROMP or an effective end-functionalization, which allows postpolymerization reactions with another block. For this purpose, numerous chain-end functionalizing agents have been reported that lead to amines,^{16,17} alcohols,¹⁸ thiols,¹⁹ or aldehydes,¹⁷ providing different possibilities of coupling reactions with distinct polymer blocks.²⁰ End-functionalized poly(norbornene) derivatives have been extensively used for the direct coupling to a hydrophilic block like polyethylene (PEG)^{21,22} or served as a macroinitiator for atom transfer radical polymerization (ATRP).^{23–25}

Interesting properties of block copolymers can be derived from blocks consisting of poly(aromatic amide)s (polyaramids). These structures are known from very resistant materials such as Kevlar. The reason for the high toughness of these

compounds is based on their molecular structure. Intramolecular hydrogen bonds and π – π stacking are responsible for these unique characteristics but also result in drawbacks such as weak solubility and hence processability. One way to overcome this disadvantage is the attachment to a solubilizing polymer, opening the door to new applications. There are only few reports on block copolymers using aramids. So far, they have been used to improve the toughness of epoxy resins,²⁶ as macroinitiators for ATRP^{27,28} or RAFT.²⁹ They have also been coupled to polyethers^{30,31} or aliphatic polyamides.³² However, aramids are highly interesting due to their ability to aggregate via the above-mentioned interactions even in the absence of solvophobic effects, thus making them promising candidates for the study of self-assembled structures.³³ Rod–coil copolymers between short oligobenzamides and solubilizing poly(ethylene glycol) chains were reported by our group previously.^{34–37} ROMP polymers have been combined with ATRP³⁸ or RAFT³⁹ as well, but to the best of our knowledge, the synthesis of a block copolymer prepared from a polyaramid and a polynorbornene block prepared by ROMP has never been reported.

Herein we report the facile synthesis of a high molecular weight block copolymer prepared via the direct coupling of poly(dimethylpropylamine norbornene imide) (PDMAPNI) and poly(dimethoxybenzyl *p*-aminobenzoate) (PArAm). The blocks were coupled by substituting the highly electrophilic pentafluorophenol (PFP) ester at the chain end of the aramid block with the amine end-functionalized poly(norbornene imide).

EXPERIMENTAL SECTION

Materials. Standard ^1H , ^{13}C , and ^{19}F nuclear magnetic resonance spectra were recorded either on a Bruker Avance III 300 at a frequency of 300 MHz (^1H) and 75 MHz (^{13}C) or at 400 MHz (^1H), 100 MHz (^{13}C), and 376 MHz (^{19}F) on a Bruker DPX 400 spectrometer. All NMR signals were referenced internally to residual solvent signals. Matrix-assisted laser desorption and ionization (MALDI) mass spectra were recorded on a Bruker ultrafleXtreme. For gel permeation chromatography in chloroform, an instrument consisting of a Duratec vacuum degasser, a KNAUER Smartline Pump 1050, and a set of two MZ-Gel SDplus linear columns (300 \times 8 mm, 5 μm particle size) was used. Signal detection occurred by use of an Applied Biosystems 759A UV detector (set to 254 nm wavelength) and a Knauer Smartline 2300 RI detector (refractive index). Calibration was done using Malvern PolycalTM UCS-PS polystyrene standards as for gel permeation chromatography in THF. The instrument is an automated Viscotek GPCmax VE-2001 with a set of two Viscotek T6000 M linear columns (300 \times 8 mm, 5 μm particle size). Signal detection occurred by use of a Viscotek Smartline 2600 UV detector (set to 254 nm wavelength) and a Viscotek VE 3580 RI detector (refractive index). Transmission electron microscopy images were recorded on a Tecnai Spirit (BioTwin lens, 120 kV LaB6 emitter) transmission electron microscope (FEL, Netherlands). To determine the manner of aggregation, sample solutions were deposited onto carbon-coated copper grids (200 mesh, Plano GmbH, Germany), which were placed on a filter paper. Samples were allowed to dry overnight protected from dust.

Solvents of analytical grade were purchased from Honeywell, Acros Organics, Sigma-Aldrich, Fisher Scientific, and Fluka and were used without further purification. Solvents of technical grade were purified by distillation, if necessary. THF (extra dry) was purchased from Sigma-Aldrich. Deuterated solvents (CDCl_3 , $\text{DMSO}-d_6$, and $\text{THF}-d_8$) were purchased from Cambridge Isotope Laboratories, Inc., or ARMAR AG. Sodium triacetoxyborohydride was purchased from FluoroChem. All further chemicals were purchased from Sigma-Aldrich, Acros Organics, or Alfa Aesar and used as received. Compounds **1** and **2** were prepared as reported previously.⁴⁰ Polymer Pre-PDMAPNI was achieved using previously reported method.⁴¹ BocNH-CTA was synthesized according to earlier reported procedure.¹⁷

Synthesis of the Poly(perfluorophenyl 4-((2,4-dimethoxybenzyl)amino)benzoate) Block (PAM Block). 4-((2,4-Dimethoxybenzyl)amino)benzoic Acid (**1**). 4-Aminobenzoic acid (1 g, 7.29 mmol) was dissolved in a tetrahydrofuran and acetic acid mixture (50:50, 14.6 mL, 0.5 M) along with 2,4-dimethoxybenzaldehyde (1.21 g, 7.29 mmol) and stirred for 10 min. Sodium triacetoxyborohydride (3.09 g, 14.58 mmol) was added portionwise to the stirring solution. After 24 h, the reaction was quenched using a solution of sodium hydrogen carbonate. The product was removed by filtration, washed with water, dried, and finally purified by column chromatography using ethyl acetate and hexane (1:3) as eluent to obtain **1** as a light yellow solid (1.9 g, 6.61 mmol, 91%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ ppm: 3.73 (s, 3 H), 3.81 (s, 3 H), 4.18 (d, J = 5.8 Hz, 2 H), 6.46 (dd, J = 8.3, 2.4 Hz, 1 H), 6.50–6.62 (m, 3 H), 6.76 (s, 1 H), 7.10 (d, J = 8.3 Hz, 1 H), 7.63 (d, J = 8.8 Hz, 2 H), 11.87 (br s, 1 H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ ppm: 55.09 (1 Cp), 55.36 (1 Cp), 97.99 (1 Ct), 104.09 (1 Ct), 110.49 (1 Ct), 116.97 (1 Cq), 118.58 (1 Cq), 128.11 (1 Ct), 131.55 (2 Ct), 152.48 (1 Cq), 157.87 (1 Cq), 159.69 (1 Cq), 167.51 (1 Cq).

Perfluorophenyl 4-((2,4-Dimethoxybenzyl)amino)benzoate (2). **1** (1.9 g, 6.61 mmol) was dissolved in dichloromethane (13.23 mL, 0.5 M) in the presence of DMAP (0.162 g, 1.32 mmol) and pentafluorophenol (1.826 g, 9.92 mmol) and cooled to 0 $^\circ\text{C}$. N,N' -Dicyclohexylcarbodiimide (1.5 g, 7.27 mmol) was added, and the solution was stirred for 5 min. The solution was then allowed to warm to room temperature and stirred overnight. The suspension was filtered, the solvent was removed, and the crude product was purified via column chromatography using ethyl acetate/hexane (1/3) as eluent. The crude product was recrystallized from ethyl acetate to give **2** as colorless crystals (1.2 g, 2.65 mmol, 36%). ^1H NMR (400 MHz,

chloroform- d) δ ppm: 3.84 (dd, J = 17.4, 0.9 Hz, 6 H), 4.36 (s, 2 H), 4.77 (br s, 1 H), 6.47 (dd, J = 8.2, 1.3 Hz, 1 H), 6.51 (d, J = 1.3 Hz, 1 H), 6.67 (d, J = 8.1 Hz, 2 H), 7.18 (d, J = 8.2 Hz, 1 H), 8.00 (d, 2 H). ^{13}C NMR (101 MHz, chloroform- d) δ ppm: 40.94 (1 Cs), 55.40 (2 Cp), 98.78 (1 Ct), 104.01 (1 Ct), 111.91 (2 Ct), 113.27 (1 Cq), 117.31 (1 Cq), 129.62 (1 Ct), 132.98 (2 Ct), 152.27 (1 Cq), 157.61 (1 Cq), 159.87 (1 Cq), 162.38 (1 Cq). ^{19}F NMR (377 MHz, chloroform- d) δ ppm: -163.83 to -161.86 (d, 2 F), -159.80 to -158.28 (t, 1 F), -152.72 (d, J = 17.7 Hz, 2 F).

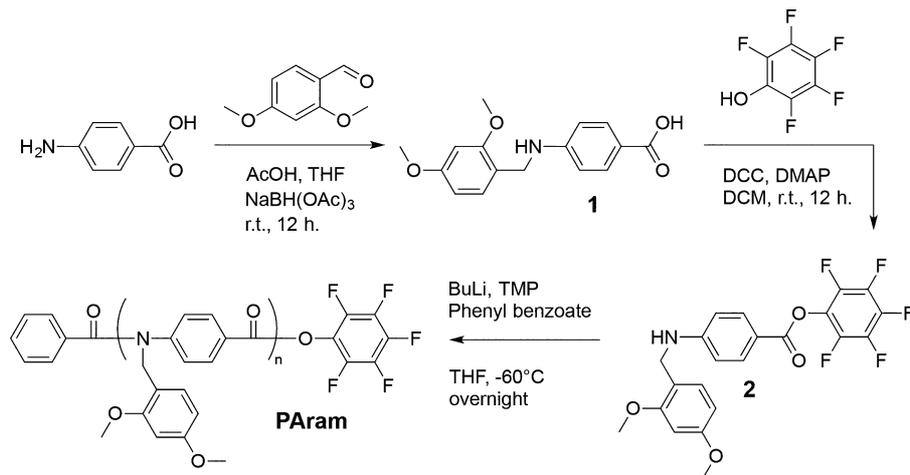
Poly(perfluorophenyl 4-((2,4-dimethoxybenzyl)amino)benzoate) (PAM). Lithium 2,2,6,6-tetramethylpiperidide (LiTMP, 3 equiv) was prepared in situ by the addition of butyllithium in hexane (0.5 mL, 1.6 M) to 2,2,6,6-tetramethylpiperidine (0.22 mL, 1.3 mmol) in THF (0.1 mL, 5 M) at -60 $^\circ\text{C}$. Phenyl benzoate (2.62 mg, 0.013 mmol) in THF (50 μL , 0.26 M) was added to LiTMP at -60 $^\circ\text{C}$ followed by the monomer **2** (120 mg, 0.265 mmol). The solution was stirred overnight at -60 $^\circ\text{C}$ before addition of a saturated solution of ammonium formate to quench the polymerization. The polymer was precipitated in ethanol. GPC (DMF, RI signal): M_n 19 800 Da/ M_w 33 500 Da/ D = 1.69. GPC (chloroform, RI signal): M_n 21 000 Da/ M_w 33 000 Da/ D = 1.52. ^1H NMR (400 MHz, chloroform- d) δ ppm: 3.46 (3 H), 3.71 (3 H), 4.95 (2 H), 6.31 (1 H), 6.36 (1 H), 6.66 (2 H), 6.98 (2 H), 7.16 (1 H).

Synthesis of the Poly(2-(3-(dimethylamino)propyl)-3a,4,7,7a-Tetrahydro-1H-4,7-methanoisindole-1,3(2H)-Dione) Amine End-Functionalized Block (PDMAPNI Block). 2-(3-(Dimethylamino)propyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-Dione (**3**). In a round-bottom flask, exonorborn-5-ene-2,3-dicarboxylic anhydride (1.0 g, 6.09 mmol) was dissolved in toluene (35 mL). 3-(Dimethylamino)-1-propylamine (1.15 mL, 9.14 mmol) was added, and the flask was equipped with a reflux condenser. The white suspension was heated to 110 $^\circ\text{C}$ for 3 h and resulted in a clear solution. Subsequently, the reflux condenser was replaced by a Claisen condenser, and the reaction was heated to 130 $^\circ\text{C}$ to remove toluene via distillation. The concentrated residue was then dissolved in dichloromethane. The organic layer was extracted three times with water before dried with anhydrous MgSO_4 . After filtration of the MgSO_4 , the solvent was evaporated under reduced pressure. The product **3** was obtained after column chromatography (10% methanol in dichloromethane) as a white solid (1.15 g, yield 76%). ^1H NMR (400 MHz, chloroform- d) δ ppm: 1.12–1.29 (m, 1 H), 1.43–1.55 (m, 1 H), 1.71 (d, J = 7.2 Hz, 2 H), 2.19 (s, 6 H), 2.24–2.38 (m, 2 H), 2.65 (d, J = 1.2 Hz, 2 H), 3.18–3.32 (m, 2 H), 3.43–3.59 (m, 2 H), 6.26 (t, 2 H). ^{13}C NMR (101 MHz, chloroform- d) δ ppm: 25.72 (1 Cs), 36.90 (1 Cs), 42.66 (1 Cs), 45.09 (2 Cp), 45.26 (2 Ct), 47.74 (2 Ct), 56.95 (1 Cs), 137.76 (2 Ct), 177.94 (2 Cq).

Poly(2-(3-(dimethylamino)propyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione) Boc-Protected Amine End-Functionalized (Pre-PDMAPNI). A sealed Schlenk flask equipped with a magnetic stir bar and monomer **3** (0.25 g, 1.01 mmol, 1 equiv) was evacuated and purged with argon three times before degassed dichloromethane (2 mL) was added via a syringe. Polymerization was initiated by fast addition of G1 (10.3 mg, 12.4 μmol) dissolved in 0.5 mL of degassed dichloromethane via syringe injection. The resulting solution was stirred for 45 min before the chain transfer agent (BocNH-CTA) (0.054 g, 0.19 mmol) dissolved in 0.7 mL of degassed dichloromethane was added quickly. The reaction was allowed to stir for 4 h after which the reaction was quenched with 1 mL of ethyl vinyl ether. The polymer was precipitated in ice-cold hexane to yield it as a white powder (0.1 g, yield 40%). The degree of end-group modification could not be determined by either ^1H NMR spectroscopy or MALDI-ToF mass spectrometry due to the high molecular weight of the sample.

Poly(2-(3-(dimethylamino)propyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione) Amine End-Functionalized (PDMAPNI). The polymer Pre-PDMAPNI (100 mg) was dissolved in THF (3 mL), and the solution was cooled to 0 $^\circ\text{C}$. 3 mL of concentrated HCl was slowly added, and the reaction was allowed to warm to room temperature and stirred overnight. THF was removed under reduced pressure, and HCl was subsequently removed under Schlenk conditions. The polymer was obtained as the HCl salt. DMF

Scheme 1. Synthetic Route to Monopentafluorophenyl Ester End-Functional Poly(aramid) PArAm



GPC, RI signal, M_n 22 000 Da/ M_w 46 000 Da/ $D = 2.11$. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 1.58 (2 H), 2.00 (2 H), 2.11 (5 H), 2.20 (2 H), 2.66 (2 H), 3.03 (2 H), 5.27–5.58 + 5.67 (2 H).

Synthesis of the Block Copolymer Poly(perfluorophenyl 4-((2,4-dimethoxybenzyl)amino)benzoate)-*b*-Poly(2-(3-(dimethylamino)propyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindole-1,3(2*H*)-dione) (PArAm-*b*-PDMAPNI). Both blocks were dissolved in $\text{DMF}-d_7$, and stirred 5 days at room temperature. The reaction was monitored using ^{19}F NMR as well as DMF GPC and showed slow conversion to the block copolymer. The block copolymer was then purified using recycling GPC in chloroform. Chloroform GPC, RI signal, M_n 27 000 Da/ M_w 43 500 Da/ $D = 1.61$. ^1H NMR (400 MHz, DMF) δ ppm: 1.22–1.59 (1 H), 1.69–1.99 (1 H), 2.39 (2 H), 3.03 (1 H), 3.24 (2 H), 3.56 (6 H), 3.68–3.82 (3 H), 3.82–3.99 (3 H), 5.19 (2 H), 6.01 (2 H), 6.66 (2 H), 7.05 (2 H), 7.25 (2 H), 7.41 (1 H).

Synthesis of the Block Copolymer Poly(perfluorophenyl 4-((2,4-dimethoxybenzyl)amino)benzoate)-*b*-Polymethylated 2-(3-(Dimethylamino)propyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindole-1,3(2*H*)-dione) (PArAm-*b*-PTMAPNI). A small drop methyl iodide was added to the block copolymer PArAm-*b*-PDMAPNI in $\text{DMF}-d_7$, and proton NMR was directly measured. The small drop methyl iodide represented already enough equivalents in order to fully quaternize the polymer. ^1H NMR (400 MHz, DMF) δ ppm: 1.17–1.62 (1 H), 1.82 (1 H), 2.39 (2 H), 2.91–3.18 (2 H), 3.24 (2 H), 3.31–3.49 (2 H), 3.56 (9 H), 3.74 (3 H), 3.90 (3 H), 5.19 (2 H), 6.01 (2 H), 6.66 (2 H), 7.05 (2 H), 7.25 (2 H), 7.41 (1 H).

RESULTS AND DISCUSSION

We recently reported the synthesis of high molecular weight aramids obtained by the controlled anionic polymerization of pentafluorophenyl (PFP) *N*-benzyl *p*-aminobenzoates.⁴⁰ We showed that those polymer chains were still bearing a PFP ester at the chain end and could, therefore, be useful for the coupling to other polymer blocks carrying a terminal nucleophile for further functionalization. This polymerization method is also interesting as it is possible to obtain very high molecular weight *N*-benzyl protected and therefore organo-soluble aramids. The cleavage of this *N*-benzyl group on the amide and thus recovery of the amide proton induces strong intermolecular hydrogen bonding which initiates aggregation. Furthermore, those hydrogen bonds combined with aromatic interactions between the polymer chains render such types of polymers insoluble in most solvents. However, in the case where block copolymers of *N*-unsubstituted aramids with *N*-alkyl-substituted aramids have been prepared, very good solubility in organic solvents can be observed.⁴²

In this report, we exploit this aggregating behavior in order to induce self-assembly between the aramid blocks. The PArAm block was obtained by polymerization of perfluorophenyl 4-((2,4-dimethoxybenzyl)amino)benzoate (**2**) which was synthesized from 4-aminobenzoic acid (Scheme 1). The synthesis pathway of the aramid monomer started with a reductive amination of the aromatic amino acid with 2,4-dimethoxybenzaldehyde using triacetoxyborohydride, which lead to product **1** (91%).⁴³ This compound was further converted to the monomer **2** via a Steglich esterification in low yield (36%) due to repeated purification cycles. Monomer **2** was then polymerized to give PArAm with a molecular weight around 20 kDa (see Scheme 1). Unfortunately, the polymer could not be analyzed by matrix-assisted-laser-desorption–ionization time-of-flight mass spectrometry (MALDI-ToF MS) due to its poor ability to get ionized. However, ^{19}F and ^1H NMR spectroscopy as well as gel permeation chromatography (GPC) in DMF and in chloroform confirmed the formation of the polymer. ^{19}F NMR spectroscopy in particular clearly showed the presence of the PFP ester at the chain end of the PArAm block (see Supporting Information), which was required for further coupling to the second nucleophilic polymer block.

In parallel to our research on the polymerization of aromatic amino acid derivatives, our group also published several methods for the end functionalization of poly(norbornene imide) using chain transfer agents.^{17–22} The monomer 2-(3-(dimethylamino)propyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindole-1,3(2*H*)-dione (**3**, 76%) was obtained by condensing *exo*-norborn-5-ene-2,3-dicarboxylic anhydride with 3-(dimethylamino)-1-propylamine and was polymerized using Grubbs' first-generation catalyst (**G1**). The protocol for the chain transfer of the poly(norbornene imide) derivative to a Boc-protected 1,4-but-2-ene diamine was published previously by our group and should lead to the Boc-protected amine end-functionalized polymer (Pre-PDMAPNI) with a molecular weight of around 20 kDa.¹⁶ Because of the high molecular weight of the polymer, end-group analysis by ^1H NMR spectroscopy or isotopically resolved MALDI-ToF mass spectrometry was unfortunately not successful. The presence of the protected amine end group was, however, indirectly shown by the successful coupling to the aramide block (see below).

The unprotected amine end-functionalized poly-(dimethylpropylnorbornene imide) (PDMAPNI) was obtained

Scheme 2. Synthetic Route to Monoamino-End-Functional ROMP Polymer PDMAPNI

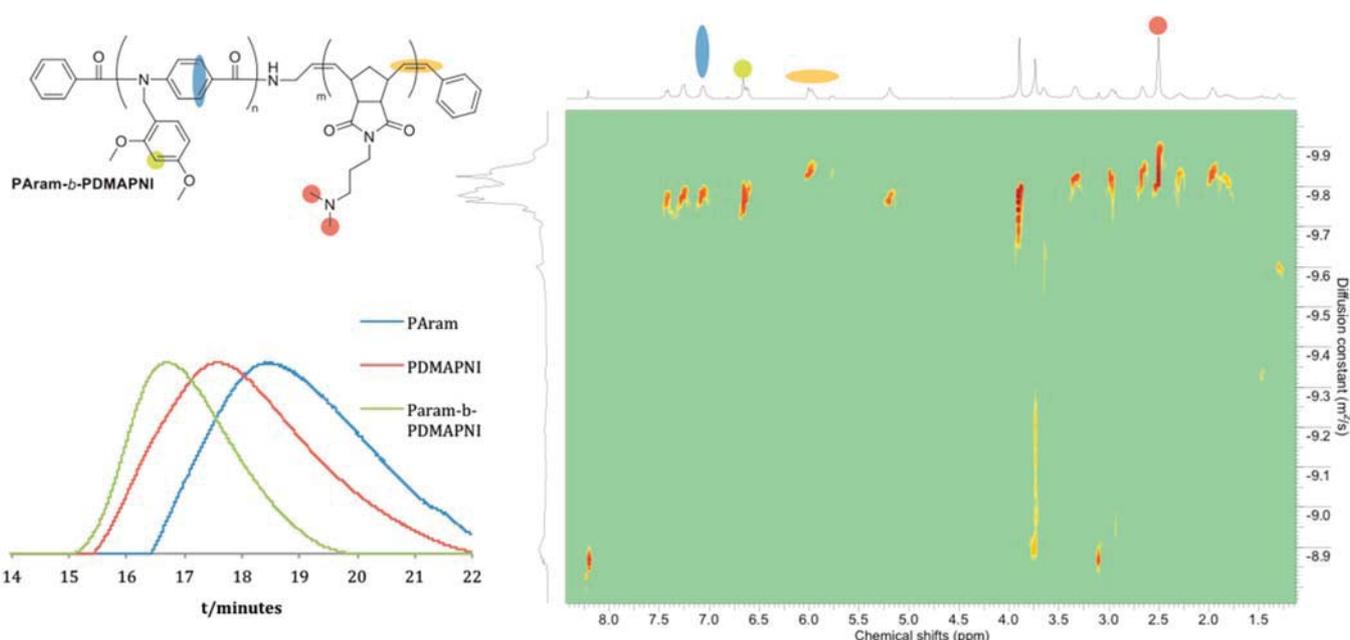
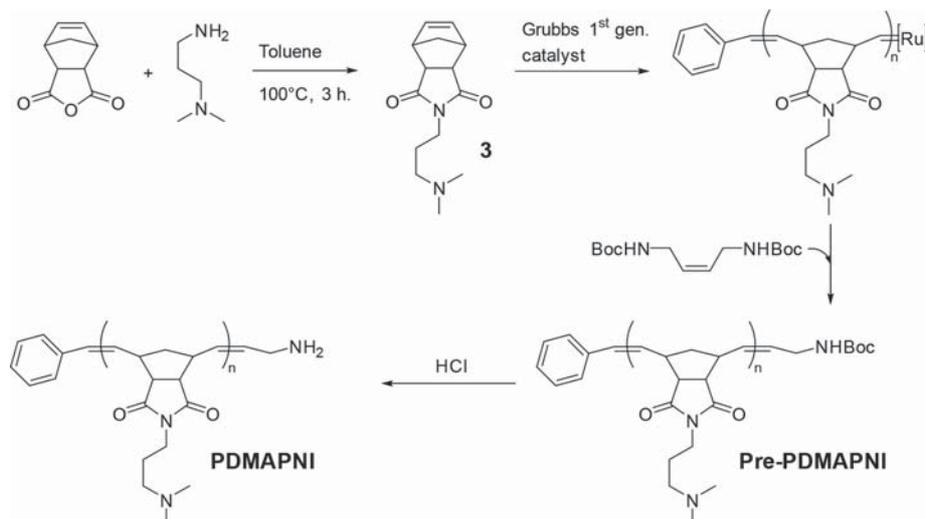


Figure 1. Left: comparison of GPC traces (RI) of the two blocks PArAm (M_n 19, M_w 33 kDa, and $\mathcal{D} = 1.7$; RI signal in DMF) and PDMAPNI (M_n 24, M_w 46 kDa, and $\mathcal{D} = 1.9$; RI signal in DMF) as well as the block copolymer PArAm-*b*-PDMAPNI (M_n 27, M_w 44 kDa, and $\mathcal{D} = 1.6$; RI signal in chloroform) after recycling GPC. Because of solubility issues, the block copolymer was measured in chloroform GPC. (For reliability of the graph, the PArAm block was measured in both DMF and chloroform GPC, resulting in comparable outcomes). Right: ^1H NMR (DMF- d_7 , 400 MHz) diffusion ordered spectroscopy (DOSY) spectrum of the block copolymer (PArAm-*b*-PDMAPNI) after recycling GPC, indicating successful coupling.

after a simple postpolymerization deprotection with hydrochloric acid solution (see Scheme 2). We believe that the broad polydispersity index ($\mathcal{D} = 2.1$) of polymer PDMAPNI, which is unusual for ROMP, is due to the presence of the amine in the monomer structure, which might coordinate to the propagating ruthenium complex and decrease the efficiency of the polymerization. Nonetheless, GPC (DMF) and ^1H NMR spectroscopy confirm the formation of a polymer of around 22 kDa molecular weight. The Boc deprotection reaction of the Pre-PDMAPNI block could unfortunately not be conclusively shown by MALDI-ToF mass spectrometry. Therefore, the Boc-deprotected polymer was analyzed only by ^1H NMR spectroscopy and GPC in DMF (see Supporting Information). Boc

deprotection could not be verified by ^1H NMR spectroscopy due to the low signal intensity of the Boc end group compared to the polymer backbone peaks. Successful deprotection was proved via the coupling to the PArAm block as clearly indicated in GPC traces (Figure 1).

The two blocks PDMAPNI and PArAm were coupled in a simple and straightforward manner upon mixing them together in DMF at room temperature for 5 days. Completion of the reaction was monitored via DMF GPC (see Supporting Information). Purification of the block copolymer PArAm-*b*-PDMAPNI was achieved using recycling GPC in chloroform, giving a copolymer of molecular weight of 27 kDa and a dispersity index of $\mathcal{D} = 1.6$ (Figure 1). Successful coupling was

Scheme 3. Synthetic Route to the Block Copolymer P*A*ram-*b*-PDMAPNI Followed by Quaternization with Methyl Iodide (ST1), Addition of Water to a Ratio of 1:1 with DMF (ST2), and Finally Cleavage of the Benzylic Amide Protecting Groups Using TFA (ST3)

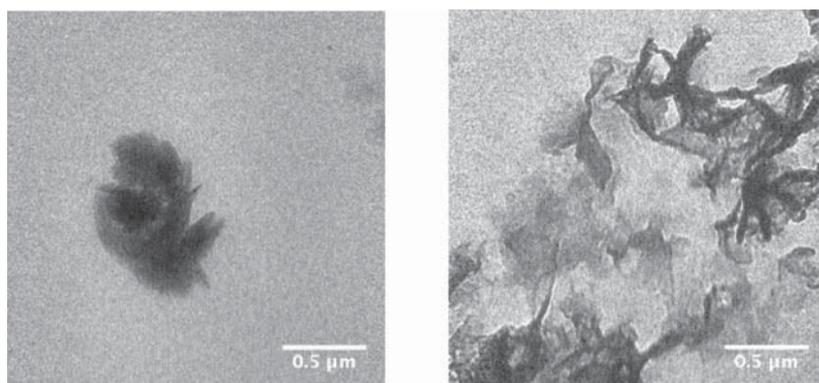
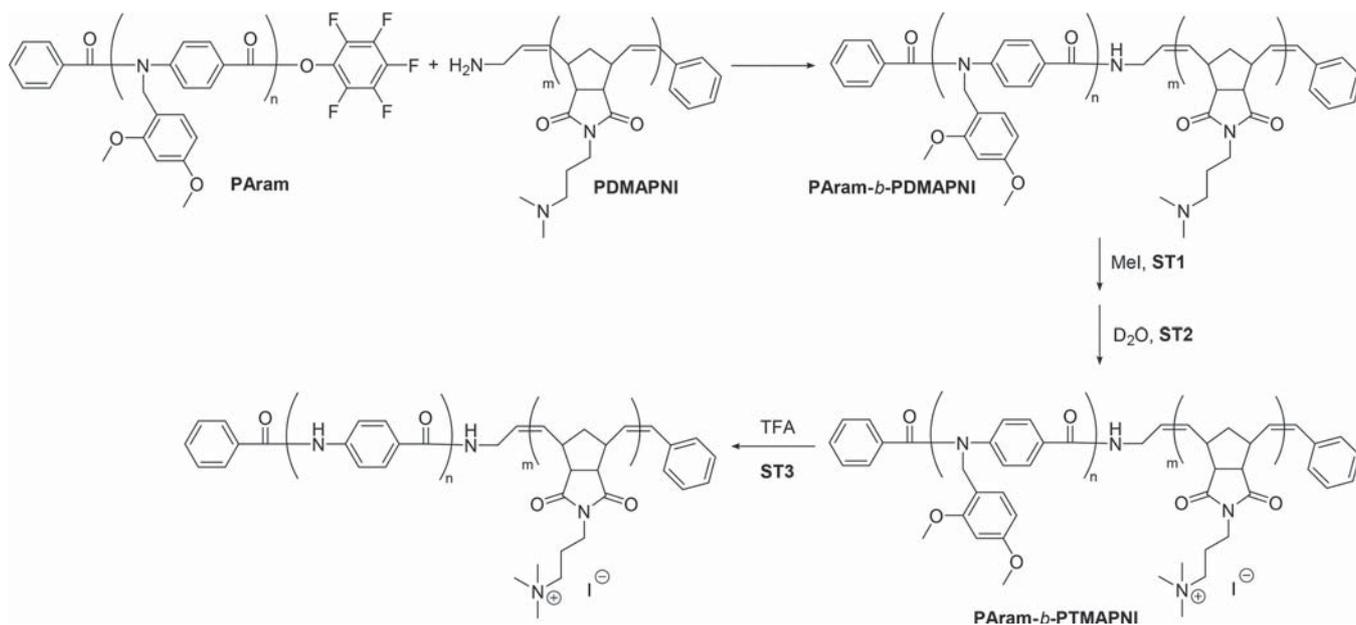


Figure 2. Transmission electron micrographs of the quaternized block copolymer P*A*ram-*b*-PTMAPNI (Scheme 3, ST2) in a deuterated mixture of DMF and water (1:1). Two different representative locations on the TEM grid show the large aggregates formed upon addition of water to the block copolymer P*A*ram-*b*-PTMAPNI in solution.

confirmed by diffusion ordered (DOSY) NMR spectroscopy (see Figure 1). Further, it was characterized by means of ^1H and ^{19}F NMR spectroscopy (see Supporting Information).

In order to induce a change in solubility of one block, and hence generate an amphiphilic character of the whole copolymer, P*A*ram-*b*-PDMAPNI was treated with methyl iodide in deuterated DMF, leading to the quaternization of the dimethylaminopropyl groups of the PDMAPNI block. At that stage of postpolymerization modification (Scheme 3, step 1, ST1, 30 mg/mL), the two blocks were still soluble and observable by ^1H NMR spectroscopy (DMF- d_7). Furthermore, no large aggregates were observed by transmission electron microscopy (TEM), even though a difference in contrast between the images of the block copolymer before and after quaternization could be observed (see Supporting Information).

Significant aggregation was induced by the addition of deuterated water to the DMF solution of P*A*ram-*b*-PTMAPNI up to a ratio of 1:1 DMF to D_2O (ST2, Scheme 3). ^1H NMR spectroscopy showed the disappearance of the hydrophobic

aromatic P*A*ram block protons, indicating signal broadening due to strong aggregation. The aromatic polyamide moiety cannot be solvated properly by this solvent mixture. The TEM images showed the formation of large aggregates of the block copolymers up to several hundred nanometers in length (Figure 2).

At this stage, we assume that the block copolymer P*A*ram-*b*-PTMAPNI (Scheme 3, ST2) adopts the shape of an amphiphilic coil-coil block copolymer. According to TEM microscopy (Figure 2, left) large aggregates are formed due to the amphiphilic nature of the diblock copolymer. As the hydrophobic effect forces the aromatic moieties to be spatially closer, aromatic interactions might take place, leading to the formation of brush or starlike aggregates (Figure 2, right). In a third step (Scheme 3, ST3), the addition of trifluoroacetic acid (TFA) cleaves the benzylic N-protecting group on the amide nitrogen and forces the aramid block to adopt a linear rodlike structure. The change of configuration of the amide bonds from *cis* to *trans* (with respect to the phenyl rings)⁴⁴ enables the formation of intermolecular hydrogen bonds in addition to the

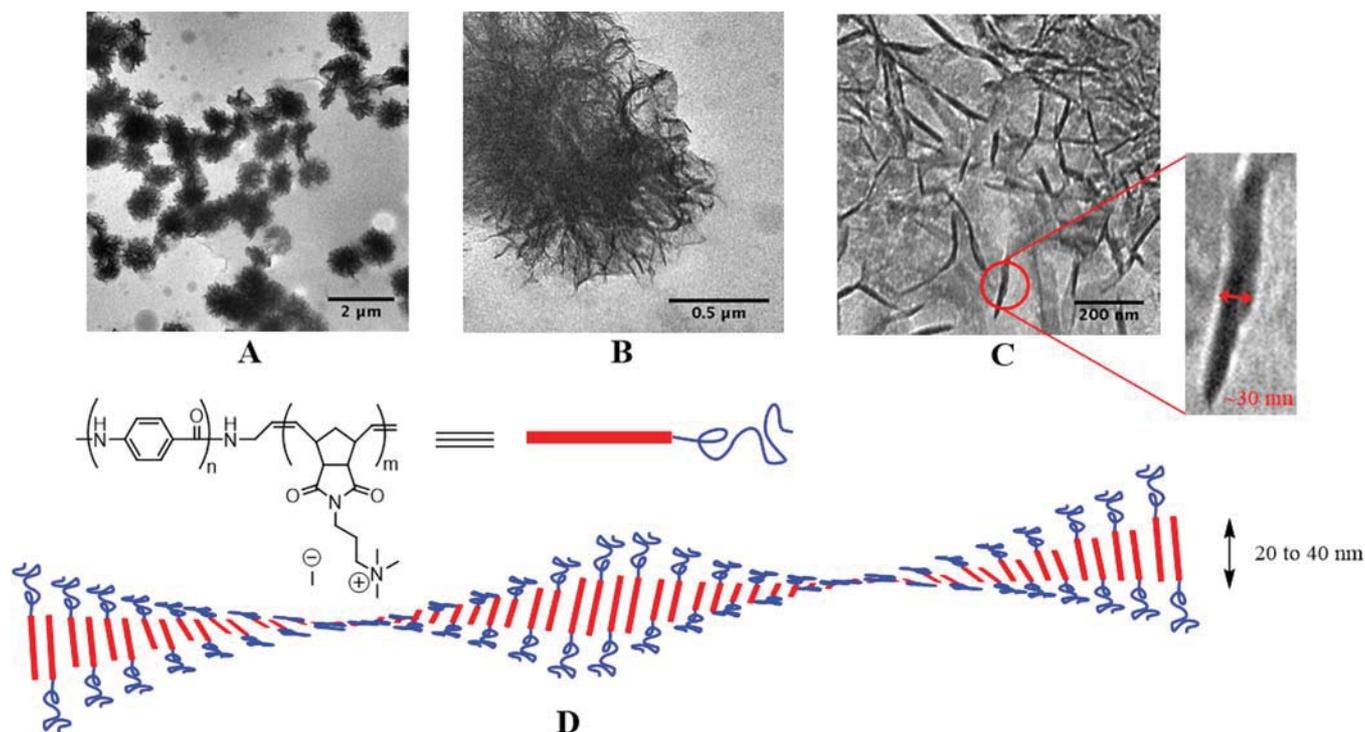


Figure 3. TEM pictures of the quaternized block copolymer PArAm-*b*-PTMAPNI after deprotection of the benzylic amide protecting groups forming “flake” like aggregates (A) consisting of agglomerated fibers (B). Zoom into an aggregate; the ribbons (of thickness from around 20 to 40 nm and with length up to 300 nm) (C) and the scheme representing the suggested alignment of the PArAm moieties with thickness from 20 to 40 nm (D).

aromatic interactions. Thus, the aramid moieties rigidify into linear rods and therefore force the block copolymer to adopt a different more well-defined shape.

The large aggregates visible in the TEM images before addition of TFA (Figure 2) are replaced by “flake”-like aggregates (Figure 3, top, A–C). These “flakes” consist of fibers with lengths from 100 to 300 nm and typical thicknesses of 20 to 40 nm, which we believe to be the ordered PArAm moieties. The greater TEM contrast of the fibers compared to the background indicates a larger electron density as it is the case for aggregated aromatic structures. Furthermore, the fibers are surrounded by diffuse areas of lower contrast that we believe to be the less electron-dense PTMAPNI chains. One linear PArAm chain of 15–20 kDa would have a length of around 35–50 nm (estimated via Chem3D molecular mechanics calculations), thus matching the width of the observed fibers. It is interesting to see that the fibers do not appear to have the same width along the contour length of the fibers. We believe that the PArAm blocks align side by side (like in the case of Kevlar) forming twisted ribbonlike structures. Because of the twisting of the ribbon, we believe that the width of the fibers might not appear constant in the projection images (Figure 3D).

The aggregation behavior of linear amide-*N*-unprotected aramid polymers has been reported before.^{34–37} However, very high molecular weight polyaramids are typically completely insoluble in common organic solvents. In the presented case, the high solubility of the charged poly(norbornene imide) derivative in a DMF/water mixture enables the aggregates to remain in solution despite the high molecular weight of the aramid block. We believe that our synthetic method allows the synthesis of even higher molecular weight polyaramid block copolymers which should self-assemble into even larger well-

defined self-assembled structures. Synthetic efforts toward such interesting nanostructures are currently underway.

■ CONCLUSIONS

In this report, we showed the facile and rapid synthesis of a block copolymer consisting of a high molecular weight aramid and a polynorbornene imide derivative block. We proved that pentafluorophenol esters, due to their high electrophilicity, are convenient end groups to build aramid block copolymers. Finally, we showed the formation of self-assemblies of a polynorbornenimide (PNI)–aramid block copolymer into ribbons with lengths up to 300 nm through postpolymerization reactions. Nanostructures were obtained following *N*-quaternization of the PNI derivative block, changing the hydrophilic character of the solvent and removal of the *N*-protecting group of the aramid block. Changing the postpolymerization modifications or their sequence could lead to several other types of arrangements and thus of other highly interesting nanostructures, which we will investigate in future reports. The potential modifications of our ROMP monomers as well as the aromatic amides are highly versatile, and a wide range of chemical functionalities can easily be incorporated into the polymer structures. The synthesis of block copolymers consisting of customizable aromatic amides and norbornene derivatives and their subsequent aggregation following the herein reported methodology provides the potential for a broad spectrum of new nano-organized macromolecules.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b01989.

Experimental procedures, ¹H and ¹³C NMR spectra, and GPC elugrams (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: andreas.kilbinger@unifr.ch (A.F.M.K.).

ORCID

Andreas F. M. Kilbinger: 0000-0002-2929-7499

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

M.B. and A.F.M.K. thank the Swiss National Science Foundation and the National Center for Competence in Research (NCCR) "Bioinspired Materials" for financial support. S.D. thanks the EU ITN "SASSYPOL" for financial support. TEM measurements (FEI Tecnai) could kindly be performed at the Adolphe-Merkle-Institute, University of Fribourg (Switzerland). The authors thank Subhajit Pal for the synthesis of a chain transfer agent.

REFERENCES

- (1) Mai, Y.; Eisenberg, A. Self-assembly of block copolymers. *Chem. Soc. Rev.* **2012**, *41*, 5969–5985.
- (2) Byard, S. J.; Williams, M.; McKenzie, B. E.; Blanazs, A.; Armes, S. P. Preparation and cross-linking of all-acrylamide diblock copolymer nano-objects via polymerization-induced self-assembly in aqueous solution. *Macromolecules* **2017**, *50*, 1482–1493.
- (3) Blanazs, A.; Armes, S. P.; Ryan, A. J. Self-assembled block copolymer aggregates: from micelles to vesicles and their biological applications. *Macromol. Rapid Commun.* **2009**, *30*, 267–277.
- (4) Antonietti, M.; Förster, S. Vesicles and liposomes: A self-assembly principle beyond lipids. *Adv. Mater.* **2003**, *15* (16), 1323–1333.
- (5) Rösler, A.; Vandermeulen, G. W. M.; Klok, H.-K. Advanced drug delivery devices via self-assembly of amphiphilic block copolymers. *Adv. Drug Delivery Rev.* **2012**, *64*, 270–279.
- (6) He, Y.; Li, Z.; Simone, P.; Lodge, T. P. Self-assembly of block copolymer micelles in an ionic liquid. *J. Am. Chem. Soc.* **2006**, *128*, 2745–2750.
- (7) Wang, X.; Guerin, G.; Wang, H.; Wang, Y.; Manners, I.; Winnik, M. A. Cylindrical block copolymer micelles and co-micelles of controlled length and architecture. *Science* **2007**, *317*, 644–647.
- (8) Kim, S. H.; Nederberg, F.; Jakobs, R.; Tan, J. P. K.; Fukushima, K.; Nelson, A.; Meijer, E. W.; Yang, Y. Y.; Hedrick, J. L. A supramolecularly assisted transformation of block-copolymer micelles into nanotubes. *Angew. Chem., Int. Ed.* **2009**, *48*, 4508–4512.
- (9) Hill, J. P.; Jin, W. S.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. Self-assembled hexa-peri-hexabenzocoronene graphitic nanotube. *Science* **2004**, *304*, 1481–1483.
- (10) Yan, D.; Zhou, Y.; Hou, J. Supramolecular self-assembly of macroscopic tubes. *Science* **2004**, *303*, 65–67.
- (11) Mokarian-Tabari, P.; Sentharamaikkannan, R.; Glynn, C.; Collins, T. W.; Cummins, C.; Nugent, D.; O'Dwyer, C.; Morris, M. A. Large block copolymer self-assembly for fabrication of subwavelength nanostructures for applications in optics. *Nano Lett.* **2017**, *17* (5), 2973–2978.
- (12) Segal-Peretz, S.; Ren, J.; Xiong, S.; Khaira, G.; Bowen, A.; Ocola, L. E.; Divan, R.; Doxastakis, M.; Ferrier, N. J.; de Pablo, J.; Nealey, P. F. Quantitative three-dimensional characterization of block copolymer directed self-assembly on combined chemical and topographical prepatterned templates. *ACS Nano* **2017**, *11*, 1307–1319.
- (13) Wang, Y.; Luo, Y.-L.; Xu, F.; Chen, Y.-S.; Tang, W. Redox-responsive PAEFC-*b*-PDMAEMA amphiphilic block copolymer self-assembly micelles: Physicochemical properties and anticancer drug controlled release. *J. Ind. Eng. Chem.* **2017**, *48*, 66–78.
- (14) Ober, C. K. Directed self-assembly: A dress code for block copolymers. *Nat. Nanotechnol.* **2017**, *12*, 507–508.
- (15) Schäfer, M.; Hanik, N.; Kilbinger, A. F. M. ROMP copolymers for orthogonal click functionalization. *Macromolecules* **2012**, *45*, 6807–6818.
- (16) Nagarkar, A. A.; Crochet, A.; Fromm, K. M.; Kilbinger, A. F. M. Efficient amine end-functionalization of living ring-opening metathesis polymers. *Macromolecules* **2012**, *45*, 4447–4453.
- (17) Nagarkar, A. A.; Kilbinger, A. F. M. End functional ROMP polymers via degradation of a ruthenium Fischer type carbene. *Chem. Sci.* **2014**, *5*, 4687–4692.
- (18) Hilf, S.; Kilbinger, A. F. M. Sacrificial synthesis of hydroxy-telechelic metathesis polymers via multiblock-copolymers. *Macromolecules* **2009**, *42*, 1099–1106.
- (19) Hilf, S.; Kilbinger, A. F. M. Thiol-functionalized ROMP polymers via Sacrificial Synthesis. *Macromolecules* **2009**, *42*, 4127–4133.
- (20) Hanik, N.; Kilbinger, A. F. M. Narrowly distributed homotelechelic polymers in 30 minutes: Using fast in-situ pre-functionalized ROMP initiators. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 4183–4190.
- (21) Hilf, S.; Hanik, N.; Kilbinger, A. F. M. A "click" approach to ROMP block copolymers. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2913–2921.
- (22) Ambade, A. V.; Yang, S. K.; Weck, M.; Supramolecular, A. B. C. triblock copolymers. *Angew. Chem., Int. Ed.* **2009**, *48*, 2894–2898.
- (23) Matson, J. B.; Grubbs, R. H. ROMP-ATRP block copolymers prepared from monotelechelic poly(oxa) norbornenes using a difunctional terminating agent. *Macromolecules* **2008**, *41*, 5626–5631.
- (24) Mahanthappa, M. K.; Bates, F. S.; Hillmyer, M. A. Synthesis of ABA triblock copolymers by a tandem ROMP-RAFT strategy. *Macromolecules* **2005**, *38*, 7890–7894.
- (25) Bielawski, C. W.; Louie, J.; Grubbs, R. H. Tandem catalysis: three mechanistically distinct reactions from a single ruthenium complex. *J. Am. Chem. Soc.* **2000**, *122*, 12872–12873.
- (26) Ochi, M.; Takemiya, K.; Kiyohara, O.; Nakanishi, T. Effect of the addition of aramid-silicone block copolymer on the phase structure and toughness of cured epoxy resins modified with RTV silicone. *Polymer* **2000**, *41*, 195–201.
- (27) Huang, C.-F.; Yokoyama, A.; Yokozawa, T. Synthesis of polybenzamide-*b*-polystyrene block copolymer via combination of chain-growth condensation polymerization and atom transfer radical polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2948–2954.
- (28) Huang, C.-F.; Ohta, Y.; Yokoyama, A.; Yokozawa, T. Efficient low-temperature atom transfer radical coupling and its application to synthesis of well-defined symmetrical polybenzamides. *Macromolecules* **2011**, *44*, 4140–4148.
- (29) Masukawa, T.; Yokoyama, A.; Yokozawa, T. Synthesis of well-defined polybenzamide-*block*-polystyrene by combination of chain-growth condensation polymerization and RAFT polymerization. *Macromol. Rapid Commun.* **2009**, *30*, 1413–1418.
- (30) Sugi, R.; Yokoyama, A.; Yokozawa, T. Synthesis of well-defined telechelic aromatic polyamides by chain-growth polycondensation: Application to the synthesis of block copolymers of polyamide and poly(tetrahydrofuran). *Macromol. Rapid Commun.* **2003**, *24* (18), 1085–1090.
- (31) Arun, A.; Gaymans, R. J. Segmented block copolymers with monodisperse amide end-segments. *Macromol. Chem. Phys.* **2008**, *209*, 854–863.
- (32) de Ruijter, C.; Mendes, E.; Boerstael, H.; Picken, S. J. Orientational order and mechanical properties of poly(amide-*block*-aramid) alternating block copolymer films and fibers. *Polymer* **2006**, *47*, 8517–8526.
- (33) Seyler, H.; Kilbinger, A. F. M. Hairy Aramide rod-coil copolymers. *Macromolecules* **2010**, *43*, 5659–5664.

(34) Schleuss, T. W.; Abbel, R.; Gross, M.; Schollmeyer, D.; Frey, H.; Maskos, M.; Berger, R.; Kilbinger, A. F. M. Hockey-Puck Micelles from Oligo(*p*-benzamide)-*b*-PEG Rod-Coil Block Copolymers. *Angew. Chem., Int. Ed.* **2006**, *45*, 2969–2975.

(35) König, H. M.; Gorelik, T.; Kolb, U.; Kilbinger, A. F. M. Supramolecular PEG-co-Oligo(*p*-benzamide)s Prepared on a Peptide Synthesizer. *J. Am. Chem. Soc.* **2007**, *129*, 704–708.

(36) Klos, J.; Wurm, F.; König, H. M.; Kilbinger, A. F. M. Automated Large-Scale Synthesis of Supramolecular Oligo(*p*-benzamide) Block Copolymers. *Macromolecules* **2007**, *40*, 7827–7833.

(37) König, H. M.; Kilbinger, A. F. M. An Improved Rapid Synthesis of Oligo(*p*-benzamide) Block Copolymers. *Macromol. Rapid Commun.* **2008**, *29*, 1721–1725.

(38) Matson, J. B.; Grubbs, R. H. ROMP–ATRP block copolymers prepared from monotelechelic poly (oxa) norbornenes using a difunctional terminating agent. *Macromolecules* **2008**, *41*, 5626–5631.

(39) Qiao, Y.; Islam, M. S.; Yin, X.; Han, K.; Yan, Y.; Zhang, J.; Wang, Q.; Ploehn, H. J.; Tang, C. Oligothiophene-containing polymer brushes by ROMP and RAFT: Synthesis, characterization and dielectric properties. *Polymer* **2015**, *72*, 428–435.

(40) Badoux, M.; Kilbinger, A. F. M. Synthesis of high molecular weight poly(*p*-benzamide)s. *Macromolecules* **2017**, *50*, 4188–4197.

(41) Nagarkar, A.; Crochet, A.; Fromm, K.; Kilbinger, A. F. M. Efficient amine end-functionalization of living ring-opening metathesis polymers. *Macromolecules* **2012**, *45*, 4447–4453.

(42) Yokozawa, T.; Ogawa, M.; Sugi, R.; Yokoyama, A. Chain-Growth Polycondensation for Well-Defined Aramide. Synthesis of Unprecedented Block Copolymer Containing Aramide with Low Polydispersity. *J. Am. Chem. Soc.* **2002**, *124*, 15158–15159.

(43) Berst, F.; Holmes, A. B.; Ladlow, M.; Murray, P. J. A latent aryl hydrazine ‘safety-catch’ linker compatible with N-alkylation. *Tetrahedron Lett.* **2000**, *41*, 6649–6653.

(44) Sisco, S. W.; Larson, B. M.; Moore, J. S. Relaxing conformation constraints in dynamic macrocycle synthesis. *Macromolecules* **2014**, *47*, 3829–3836.