Facile synthesis of a high molecular weight amphiphilic aramid-ROMP block copolymer.

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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) (PDMNI) and a pentafluorophenol ester terminated poly(dimethoxybenzyl para-aminobenzoate) (PAram). Post-polymerization amide *N*-deprotection of the block copolymer yielded a strongly aggregating water soluble rod-coil copolymer. Transmission electron microscopy revealed the formation of large ribbon-like aggregates with sizes up to 50 nanometers in thickness and 300 nanometers in length.

Introduction

Over the last decades, many efforts have been directed towards 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[5,6,7] to nanotubes[8,9,10] 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 blocks[15] 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 post-polymerization 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 macro-initiator for atom transfer radical polymerization (ATRP).[23,24,25]

Interesting properties of block co-polymers can be derived from blocks consisting of poly aromatic amides (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. Intra-molecular 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 macro initiators 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 polyethylene glycol chains were reported by our group previously.[34,35,36,37] ROMP polymers have been combined with ATRP[38] or RAFT[39] 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 co-polymer prepared via the direct coupling of poly(dimethylpropylamine norbornene imide) (**PDMAPNI**) and poly(dimethoxybenzyl *para*-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 ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance spectra were recorded either on a Bruker Avance III 300 at a frequency of 300 MHz (^{1}H) and 75 MHz (^{13}C) or at 400 MHz (^{1}H), 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 x 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 Polycal™ 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 T6000M linear columns (300 x 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 (FEI, 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$_3$, DMSO-d$_6$, 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 (**PAram** 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 minutes. Sodium triacetoxyborohydride (3.09 g, 14.58 mmol) was added portion wise to the stirring solution. After 24 hours, 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%). ^{1}H NMR (300 MHz, 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, 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°C. N,N'-Dicyclohexylcarbodiimid (1.5 g, 7.27 mmol) was added and the solution was stirred for 5 minutes. The solution was then allowed to warm to room temperature and stirred overnight. The suspension was filtered, the solvent 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%). ^{1}H 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 - -161.86 (d, 2 F) -159.80 - -158.28 (t, 1 F) -152.72 (d, J=17.7 Hz, 2 F).

Poly(perfluorophenyl 4-((2,4-dimethoxybenzyl)amino) benzoate) (**PAram**).

Lithium 2,2,6,6-tetramethylpiperidide (LiTMP, 3 eq.) was prepared in situ by the addition of butyl lithium 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°C. Phenyl benzoate (2.62 mg, 0.013 mmol) in THF (50µl, 0.26 M) as the initiator was added to LiTMP at -60°C followed by the monomer **2** (120 mg, 0.265 mmol). The solution was stirred over night at -60°C before addition of a saturated solution of ammonium formate to quench the polymerization. The polymer was precipitated in ethanol. GPC (DMF, RI signal): Mn 19'800 Da / Mw 33'500 Da / Đ= 1.69. GPC (chloroform, RI signal): Mn 21'000 Da / Mw 33'000 Da / Đ= 1.52. ^{1}H 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-methanoisoindole-1,3(2H)-dione) amine end functionalized block (**PDMAPNI** block).*

2-(3-(dimethylamino)propyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (**3**).

In a round bottom flask, exo-norborn-5-ene-2,3-dicarboxylic anhydride (1.0 g, 6.09 mmol) was dissolved in toluene (35 mL). 3-(Dimethylamino)-1-propylamine (1.15mL, 9.14mmol) was added and the flask was equipped with a reflux condenser. The white suspension was heated to 110°C for 3h and resulted in a clear solution. Subsequently, the reflux condenser was replaced by a Claisen-condenser and the reaction was heated to 130°C to remove toluene via distillation. The concentrated residue was then dissolved in dichloromethane. The organ-

2

ic 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, yield 76%). ^{1}H 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-methanoisoindole-1,3(2H)-dione) Boc protected amine end functionalized (**Pre-PDMAPNI**).

A sealed Schlenk flask equipped with a magnetic stir bar and monomer **3** (0.25g, 1.01mmol 1 eq) was evacuated and purged with argon three times before degassed dichloromethane (2mL) was added via a syringe. Polymerization was initiated by fast addition of G1 (10.3mg, 12.4μmol) dissolved in 0.5mL degassed dichloromethane via syringe injection. The resulting solution was stirred for 45min before the chain transfer agent (**BocNH-CTA**) (0.054g, 0.19mmol) dissolved in 0.7mL degassed dichloromethane was added quickly. The reaction was allowed to stir for 4h after which the reaction was quenched with 1mL ethyl vinyl ether. The polymer was precipitated in ice-cold hexane to yield it as a white powder (0.1g, yield: 40%). The degree of end group modification could not be determined by either ^{1}H-NMR spectroscopy of 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-methanoisoindole-1,3(2H)-dione)   amine   end   functionalized (**PDMAPNI**).

The polymer **Pre-PDMAPNI** (100mg) was dissolved in THF (3mL) and the solution was cooled to 0°C. 3ml 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 GPC, RI signal, Mn 22'000 Da / Mw 46'000 Da / Đ= 2.11. ^{1}H NMR (400 MHz, 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)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione) (**PAram**-b-**PDMAPNI**).*

Both blocks were dissolved in 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 co-polymer was then purified using recycling GPC in chloroform. Chloroform GPC, RI signal, Mn 27'000 Da / Mw 43'500 Da / Đ= 1.61. ^{1}H 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*- poly methylated (2-(3-(dimethylamino)propyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione) (**PAram**-*b*-**PTMAPNI**).

A small drop methyl iodide was added to the block copolymer **PAram**-*b*-**PDMAPNI** in 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. ^{1}H 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 *para*-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 organosoluble aramids. The cleavage of this *N*-benzyl group on the amide and thus recovery of the amide proton induces strong inter-molecular hydrogen bonding which initiate 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 [1]H

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 info), which was required for further coupling to the second nucleophilic polymer block.

Scheme 1. Synthetic route to mono pentafluorophenyl ester end functional polyaramid Param.
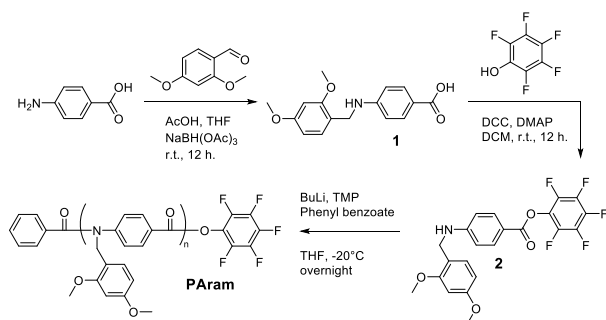
In parallel to our research on the polymerization of aromatic amino acid derivatives, our group also published several methods for the end functionalization of poly(norbornene imide) using chain transfer agents.[17,18,19,20,21,22] The monomer 2-(3-(dimethylamino)propyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (**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] Due to the high molecular weight of the polymer, end group analysis by ^{1}H-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(dimethylpropyl norbornene imide) (**PDMAPNI**) was obtained after a simple post-polymerization deprotection with hydrochloric acid solution (see Scheme 2). We believe that the broad poly dispersity index (Đ=2.1) of polymer **PDMAPNI**, which is unusual for ROMP, is due to the presence of the amine in the monomer structure, that might coordinate to the propagating ruthenium complex and decrease the efficiency of the polymerization. Nonetheless, GPC (DMF) and ^{1}H-NMR spectroscopy confirm the formation of a polymer of around 22kDa molecular weight. The Boc deprotection reaction of the **PAram** block could unfortunately not be conclusively shown by MALDI-ToF mass spectrometry. Therefore, the Boc deprotected polymer was analyzed only by ^{1}H NMR spectroscopy and GPC in DMF (see supporting info). Boc-deprotection could not be verified by ^{1}H 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).

**Scheme 2.** Synthetic route to mono amino-end-functional ROMP polymer **PDMAPNI**.
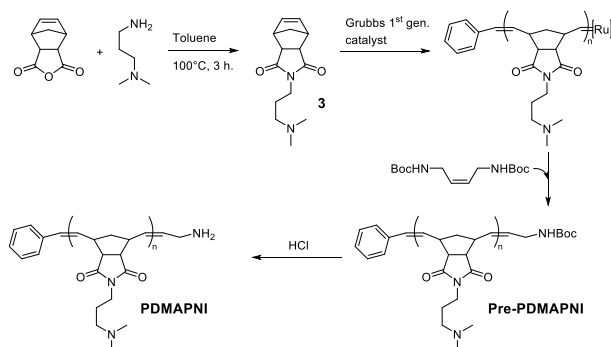
The two blocks **PDMAPNI** and **PAram** were coupled in a simple and straightforward manner upon mixing them together in DMF at room temperature for 5 d. Completion of the reaction was monitored via DMF GPC (see supporting info). Purification of the block copolymer **PAram**-*b*-**PDMAPNI** was achieved using recycling GPC in chloroform, giving a copolymer of molecular weight of 27 kDa and a dispersity index of Đ=1.6 (Figure 1). Successful coupling was confirmed by Diffusion Ordered (DOSY) NMR spectroscopy (see Figure 1). Further, it was characterized by means of ^{1}H and ^{19}F NMR spectroscopy (see supporting info).

In order to induce a change in solubility of one block, and hence generate an amphiphilic character of the whole copolymer, **PAram**-*b*-**PDMAPNI** was treated with methyl iodide in deuterated DMF, leading to the quaternization of the dimethyl amino propyl groups of the **PDMAPNI** block. At that stage of post-polymerization modification (Scheme 3 Step 1, ST1, 30 mg/mL), the two blocks were still soluble and observable by ^{1}H 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 info).
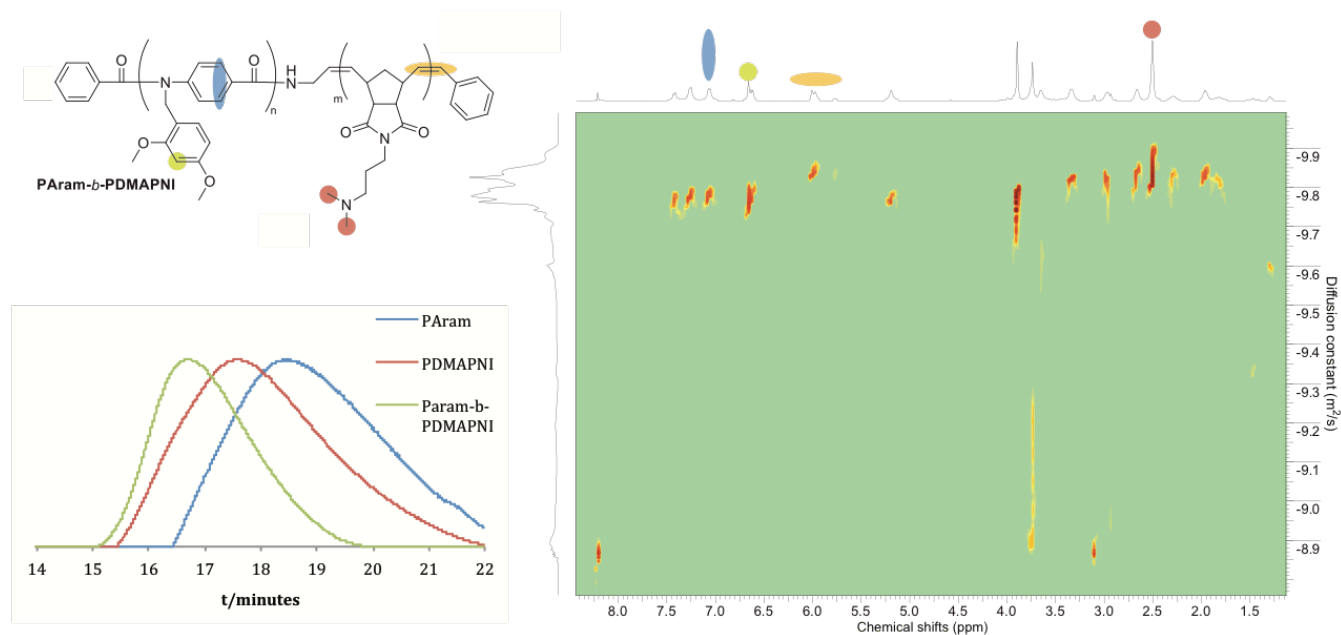

Figure 1. Left: Comparison of GPC traces (RI) of the two blocks **PAram** (Mn 19, Mw 33 kDa and Đ= 1.7; RI signal in DMF) and **PDMAPNI** (Mn 24, Mw 46 kDa and Đ= 1.9; RI signal in DMF) as well as the block copolymer **PAram**-*b*-**PDMAPNI** (Mn 27, Mw 44 kDa and Đ= 1.6; RI signal in chloroform) after recycling GPC. Due to 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: ^{1}H NMR (DMF-d[7], 400MHz) Diffusion Ordered Spectroscopy (DOSY) spectrum of the block copolymer (**PAram**-*b*-**PDMAPNI**) after recycling GPC indicating successful coupling.

Significant aggregation was induced by the addition of deuterated water to the DMF solution of **PAram**-*b*-**PTMAPNI** up to a ratio a of 1:1 DMF to D[2]O (ST2, Scheme 3). ^{1}H NMR spectroscopy showed the disappearance of the hydrophobic aromatic **PAram** 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).
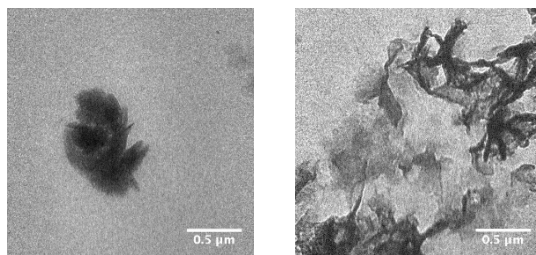
Figure 2. Transmission Electron Micrographs of the quaternized block copolymer **PAram**-*b*-**PTMAPNI** (Scheme 3 ST2) in a deuterated mixture of DMF and water (1:1). Two different, representative locations on the TEM grid show the large aggregates formed upon addition of water to the block copolymer **PAram**-*b*-**PTMAPNI** in solution.

Scheme 3. Synthetic route to the block copolymer **PAram-*b*-PTMAPNI** 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).
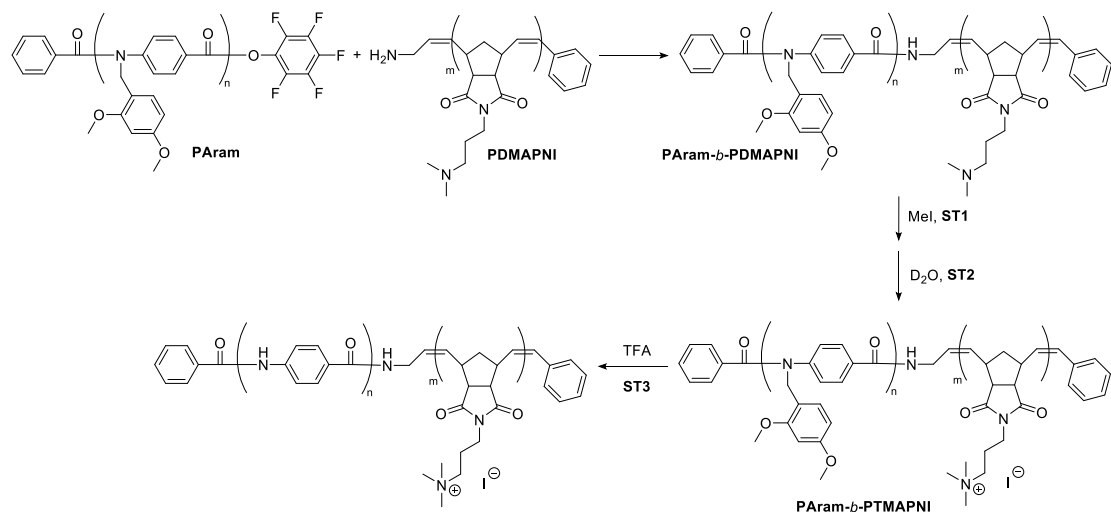
At this stage, we assume that the block copolymer **PAram-b-PTMAPNI** (Scheme 3 ST2) adopts the shape of an amphiphilic coil-coil block copolymer. According to TEM microscopy (Figure 2, left) large aggregates are formed due to the amphiphilic nature of the diblock copolymer. As the hydrophobic effect forces the aromatic moieties to be spatially closer, aromatic interactions might take place, leading to the formation of brush or star like 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 rod-like 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 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 50 nm, that 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 to 20 kDa would have a length of around 35 to 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 ribbon-like structures. Due to the twisting of the ribbon, we believe that the width of the fibers might not appear constant in the projection images (Figure 3, D).

The aggregation behavior of linear amide-*N*-unprotected aramid polymers has been reported before.[34,35,36,37] 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-blockcopolymers which should self-assemble into even larger well-defined self-assembled structures. Synthetic efforts towards such interesting nano-structures are currently underway.
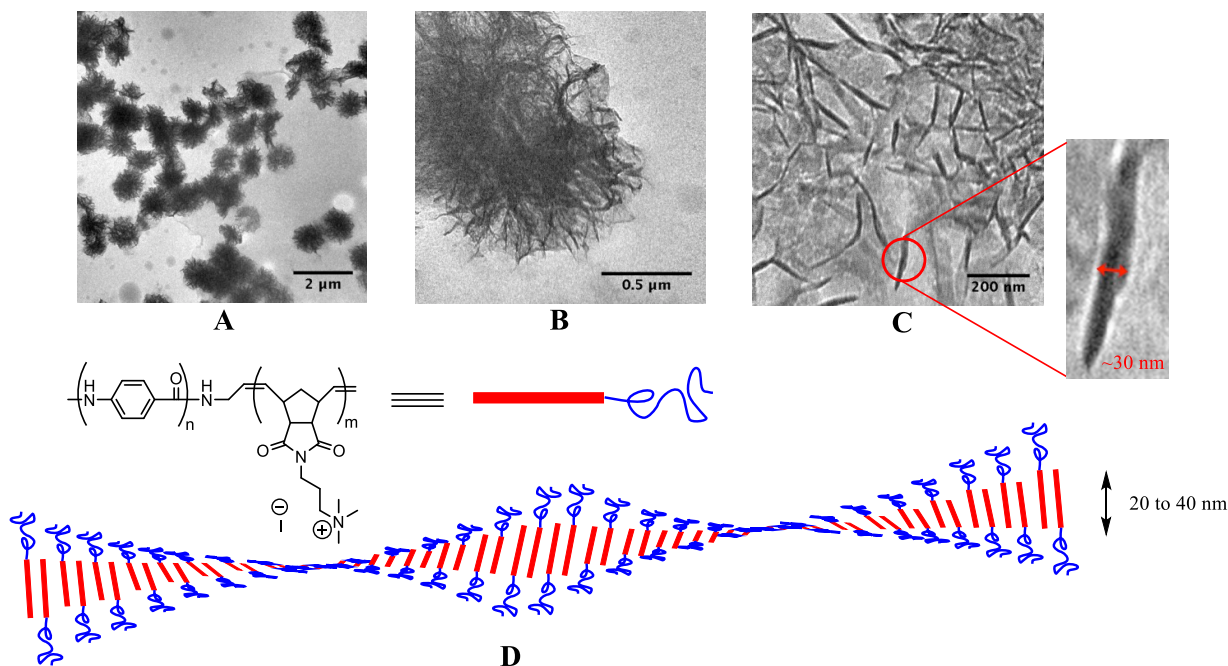
Figure 3. TEM pictures of the quaternized block copolymer **PAram**-*b*-**PTMAPNI** after deprotection of the benzylic amide protecting groups forming "flake" like aggregates (A) consisting of agglomerated fibers (B). Zoom into an aggregate; the ribbons (of thickness from around 20 to 45 nm and with length up to 300 nm) (C) and the Scheme representing the suggested alignment of the **PAram** moieties with thickness from 20 to 45 nm (D).

Conclusions

In this report, we showed the facile and rapid synthesis of a block copolymer consisting of a high molecular weight aramid and a poly norbornene 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 post-polymerization 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 post-polymerization 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 is 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.

Experimental procedures,^{1}H, ^{13}C-NMR spectra and GPC elugrams.

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