Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 5659–5664 **5659**
DOI: 10.1021/ma100230z

Hairy Aramide Rod−Coil Copolymers

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Received January 29, 2010; Revised Manuscript Received April 29, 2010

ABSTRACT: We have synthesized monodisperse "hairy rod oligomers" based on oligo(*p*-benzamide)s carrying alkyl side chains and conjugated them with polydisperse poly(ethylene glycol) (PEG) chains. The well-defined oligomers were synthesized from 4-amino-2-hexyloxybenzoic acid using a commercial peptide synthesizer. The PEG conjugated hairy rod−coil block copolymers self-assemble in polar and nonpolar organic solvents. The self-organization in solution was investigated by dynamic light scattering (DSL) and transmission electron microscopy (TEM) as a function of solvent, equilibration time, and polarity of the substrate. Individual fibers and fiberlike bundles of aggregates could be observed. As all hydrogen bond donors are intramolecularly saturated in these aramide oligomers, we propose π-stacking as the aggregation mechanism for this novel class of substituted oligoaramides. NMR studies on a model compound support this assumption.

Introduction

"Hairy rods"[1] (HR) are stiff rigid-rod-like oligomers or polymers to which flexible short or long side chains are attached. These "liquidlike" substituents often act like a polymer bound solvent shell, disguise the backbone, and in most cases help to achieve higher solubility and easier processability.[2] This class of polymeric materials has a high tendency to self-assemble into interesting supramolecular structures,[3,4] in both bulk and solution. Thin films prepared from hairy rods often exhibit high dimensional stability since the rigid backbones act as reinforcing elements in an amorphous matrix of side chains,[5] overcoming compatibility limitations in some composite materials.[4] Hairy rods can also show liquid crystalline properties[6] and have received significant attention in the context of electrically conductive architectures, when the main chain, i.e., the backbone, consists of π-conjugated rigid polymers.[7]

Typical polymers and oligomers that belong to this class of materials are substituted polyglutamates,[1,8] polyalkylthiophenes,[9,10] substituted poly-*p*-phenylenes,[4,11] and polyfluorenes.[10,12]

Because of the precedence in π-conjugated polymers and oligomers, applying the concept of "hairy rods" to aromatic amides seemed very promising to us. Introducing alkyloxy side chains to aromatic oligoamides has been used by many groups as a tool to rigidify the oligomer backbone via hydrogen bonds. Such rigidifications often result in thermodynamically favored molecular shapes. Hydrogen bonds have been used in the design of helices and in the preorganization of beta strands, macrocycles, and rigid linear structures.[13]

Various syntheses of oligo(*p*-benzamide)s (OPBA) that do not carry alkyloxy side chains have been described, and their hydrogen bond driven superstructures observed in solution have been investigated in detail.[14] Few reports so far have described the introduction of alkyloxy side chains to linear oligo(*p*-benzamide)s.[15,16] We recently described the synthesis of short ethylene oxide side chains attached to a rigid poly(*p*-benzamide) chain which leads to a highly processable and organo-soluble polymeric material.[15] On the other hand, a high density of *n*-hexyloxy substituents attached to the rigid oligo(*p*-benzamide) rod was shown to induce the opposite effect, i.e., insolubility. The fact, that *n*-hexyloxy substituents on oligo(*p*-benzamide)s lead to lower solubility compared to the unsubstituted oligomer is counterintuitive at first. In order to "solubilize" these hairy *n*-hexyloxy-substituted linear nano-objects, we conjugated the well-defined oligomers to solubilizing PEG chains.

Here we describe how 2-*n*-hexyloxy substituents in oligo(*p*-benzamide)s can be used to synthesize strongly aggregating copolymers and report how the introduction of such substituents can be employed as a facile tool to increase noncovalent interactions in oligo(*p*-benzamide) systems.

Experimental Part

Methods. Standard ^{1}H nuclear magnetic resonance spectra were recorded on a Bruker AMX 400 (400 MHz). Infrared spectra were recorded on a Nicolet 5 DXC FT-IR spectrometer. ESI mass spectra were measured on a Micromass Q-TOF Ultima 3. RP-HPLC analysis was performed on a Hewlett-Packard HP 1090 liquid chromatograph equipped with PerfectSil column (MZ Analysentechnik, Mainz, Germany, 250 × 4.0 mm; 120 ODS-2 5 mm). The samples were eluted with an acetonitrile/water gradient that started from 10% acetonitrile rising to 90% over a period of 35 min and maintained constant for additional 10 min. Both solvents were buffered with 0.1% TFA. UV-detection was performed at 254 nm.

Dynamic light scattering (DLS) experiments were performed at 293 K utilizing equipment consisting of a He/Ne laser (λ = 632.8 nm), an ALV 3000 correlator, and an ALV-SP86 goniometer. Measurements were performed at different angles (for most samples between 30° and 120°, in 15° steps). Diffusion coefficients were determined by nonlinear fitting (simplex algorithm) of the field autocorrelation function applying biexponential fit functions. Hydrodynamic radii were calculated by applying the Stokes−Einstein equation. All solutions were passed through syringe filters (Anotop, 20 nm) into dust-free cylindrical cuvettes.

A Philips EM 420 transmission electron microscope using a LaB_6 cathode at an acceleration voltage of 120 kV was used to obtain TEM images. Hydrophilization of the TEM grids (carbon film on copper, 300 mesh) was carried out for 30 s in

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Published on Web 06/04/2010

a plasma (O_2) cleaner. The samples were prepared by the drop-cast method, air-dried, and stained with OsO_4.

Gel permeation chromatography with chloroform was carried out on an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, and a set of three PSS SDV columns ($10^6/10^5/10^4$ g/mol). Signal detection was performed with a TSP Spectra System UV 2000 (UV 254 nm) and a Wyatt Optilab DSP (refractive index).

Ab initio calculations were carried out on Spartan 08 parallel, version 1.2.0, Wavefunction, Inc., Irvine, CA. The hairy rod oligomers were synthesized on an ABI 431A peptide synthesizer using adapted synthetic procedures similar to those described earlier.[17]

Reagents and Materials. All solvents and reagents were purchased from Aldrich unless otherwise stated. Poly(ethylene glycol) monomethyl ether was purchased from Fluka. *N*-Fmoc-4-amino-2-hexyloxybenzoic acid was synthesized as reported earlier[15] and converted into the corresponding acid chloride (**3**) using thionyl chloride and *N*-methyl-2-pyrrolidone (NMP).

The conversion of the PEG monomethyl ether into the PEG carboxylic acid as well as the attachment of the PEG-blocks to the oligoamides on the solid support was accomplished as described previously.[14d]

General Activation Method (*GM1*). The corresponding benzoic acid derivative was dissolved in thionyl chloride under an argon atmosphere, followed by the addition of a catalytic amount of dry NMP. The reaction mixture was allowed to react for 2 h at room temperature. Thionyl chloride was then removed under reduced pressure, the crude acid chloride was dissolved in dry dichloromethane (DCM), and the solvent was removed under reduced pressure. The resulting solid was redissolved in dry NMP, and the freshly prepared solution was used for the automated solid supported synthesis of the oligoamides.

General Description of the Automated Solid Supported Oligoamide Synthesis. Cycles of *N*-Fmoc deprotection, monomer coupling, and N-capping reaction steps were sequentially carried out on the peptide synthesizer. The functionalized resin was either treated with TFA in order to isolate the final oligomer or further used for the preparation of the block copolymers.

General Method for the Preparation of the Block Copolymers (*GM2*). Poly(ethylene glycol) monomethyl ether carboxylic acid (PEG2000-COOH, molecular weight 2000 g mol^{-1}, degree of polymerization ca. 44) was converted into the acid chloride derivative (PEG2000-COCl) using oxalyl chloride in DCM. After 3−4 h reaction time, the excess of oxalyl chloride and the solvent were removed under reduced pressure. The crude product was then dissolved in a minimum amount of NMP and added to the previously swollen functionalized resin. The mixture was agitated for 24 h, filtrated and washed subsequently with NMP and DCM, and dried. The described procedure was repeated once. The block copolymer was cleaved from the resin using 50 vol % TFA in DCM for 2 h at room temperature.

*Trimer **4a***. *N*-Fmoc-4-amino-2-hexyloxybenzoic acid (2.3 g, 5 mmol) was converted into the acid chloride **3** in 12.5 mL of $SOCl_2$ following the GM1 procedure. Compound **3** and 4-nitrobenzoyl chloride (0.69 g, 3 mmol) were dissolved in 9.4 and 5.5 mL of dry NMP, respectively, for the automated solid phase synthesis (coupling and N-capping solutions). The cleavage from the resin was perfomed in 6 mL of 50 vol % TFA in DCM for 2 h. The crude trimer **4a** was precipitated in diethyl ether and purified by rinsing with hot chloroform (yield: 120 mg, 71%).

^{1}H NMR δ (400 MHz, $CDCl_3$/MeOD (20 vol % MeOD in $CDCl_3$)): 0.83 (t, 9 H, ^3J = 6.52 Hz); 1.23−1.49 (m, 18 H); 1.82−1.95 (m, 6 H); 4.06 (t, 2 H, ^3J = 6.36 Hz); 4.21 (t, 4 H, ^3J = 6.52 Hz); 6.17 (d, 1 H, ^4J = 1.27 Hz); 6.30 (dd, 1 H, ^4J = 1.91 Hz, ^3J = 8.58 Hz); 6.68 (dd, 1 H, ^4J = 1.59 Hz, ^3J = 8.58 Hz); 6.72 (dd, 1 H, ^4J = 1.59 Hz, ^3J = 8.58 Hz); 7.91 (d, 1 H, ^3J = 8.58 Hz); 7.96 (d, 1 H, ^3J = 8.58 Hz); 8.01−8.07 (m, 3 H).

^{1}H NMR δ (300 MHz, DMSO-d_6): 0.80−0.90 (m, 9 H); 1.23−1.46 (m, 18 H); 1.71−1.93 (m, 6 H); 4.0 (t, 2 H, ^3J = 6.36 Hz); 4.10 (m, 4 H); 6.27 (dd, 1 H); 6.29 (d, 1 H); 7.24 (dd, 1 H, ^4J = 1.27 Hz, ^3J = 8.58 Hz); 7.29 (dd, 1 H, ^4J = 1.27 Hz, ^3J = 8.58 Hz); 7.54 (s, 1 H); 7.65−7.75 (m, 4 H); 10.07 (s, 1 H); 10.16 (s, 1 H).

MS (ESI): m/z (%) = 698.39 (100); 699.41 (3.7); calcd $(M + Na)^+$ $[C_{39}H_{53}N_3O_7Na]^+$ = 698.38.

*Tetramer **4b***. *N*-Fmoc-4-amino-2-hexyloxybenzoic acid (3.59 g, 7.8 mmol) was converted into the acid chloride **3** in19.5 mL of $SOCl_2$ following the GM1 procedure. Compound **3** and 4-nitrobenzoyl chloride (0.97 g, 5.2 mmol) were dissolved in 15 and 7 mL of dry NMP, respectively (coupling and *N*-capping solutions) and were used in the automated synthesis of the tetramer functionalized resin **4b***.

*Block Copolymer **5b***. The poly(ethylene glycol) activation was performed following the GM2 procedure using 2.5 g of PEG2000-COOH, 10 mL of oxalyl chloride, and 10 mL of dry DCM. The PEG2000-COCl was then reacted with the functionalized resin **4b*** (0.25 mmol) to obtain 253 mg of crude product (ca. 28%). An analytical sample (50 mg) was purified by preparative GPC in chloroform, affording 37 mg of pure **5b**.

GPC (chloroform): M_n = 4850 g/mol; M_w = 5440 g/mol; PDI = 1.12.

^{1}H NMR: δ (300 MHz, $CDCl_3$): 0.92−0.95 (m, 12 H); 1.38−1.59 (m, 24 H); 1.85−2.01 (m, 8 H); 3.37 (s, 3 H); 3.65 (br. s, 151 H); 4.29 (br. s, 8 H); 5.05 (br s; 4 H); 6.54−7.01 (m, 3 H); 7.75−9.89 (m, 9 H); 9.84−10.36 (m, 3 H).

*Heptamer **4c***. *N*-Fmoc-4-amino-2-hexyloxybenzoic acid (5.98 g, 13 mmol) was converted into the acid chloride **3** in 32.5 mL of $SOCl_2$ following the GM1 procedure. Compound **3** and 4-nitrobenzoyl chloride (1.6 g, 8.6 mmol) were dissolved in 24.4 and 13 mL of dry NMP, respectively (coupling and N-capping solutions) and were used in the automated synthesis of the tetramer functionalized resin **4c***.

*Block Copolymer **5c***. The poly(ethylene glycol) activation was performed following the GM2 procedure using 2.5 g of PEG2000-COOH, 5 mL of oxalyl chloride, and 5 mL of dry DCM. The PEG2000-COCl was then reacted with the functionalized resin **4c*** (0.25 mmol). A resin sample (108 mg) was exposed to the TFA/DCM solution, affording 55 mg (75%) of an off-white solid.

IR: 3340, 2928, 2860, 1670, 1578, 1521, 1239, 1127, 1103.

Purification/characterization: It was impossible to purify the product with standard chromatographic methods or precipitation due to its very high aggregation tendency. The characterization by NMR, GPC, HPLC, and mass spectrometry techniques failed, making it impossible to estimate the purity level of the afforded product.

Solubility of crude **5c**: good solubility in chloroform and HFIP; poorly soluble in DMSO and DMF; insoluble in acetonitrile, methanol, and water.

Results and Discussion

We previously reported the synthesis of hepta(2-hexyloxy-*p*-benzamide) (**1**) carrying *n*-hexyloxy substituents on every aromatic repeat unit (Figure 1).[15] To our surprise, compound **1** was completely insoluble in all common organic solvents available in our laboratory. We hence speculated that this insolubility arose from a rigidification of the oligo(*p*-benzamide) backbone induced by the intramolecular hydrogen bonds between the amide N−H and the ether oxygen (see Figure 1). *Ab initio* calculations (MP2 6-31G*) of a model compound carrying methoxy instead of hexyloxy substituents (hepta(2-methoxy-*p*-benzamide), **2**; see Figure 1) confirmed the existence of intramolecular hydrogen bonds and predicted a perfectly coplanar arrangement of all phenyl rings in the oligomer (Figure 1). This "flattening" of the oligomer, together with the intramolecular saturation of the N−H hydrogen bond donors, leads to a change in aggregation mechanism from hydrogen bond driven for the unsubstituted case to π-interactions (i.e., weak electrostatic interactions) for the alkyloxy-substituted ones. Similar observations have already been reported

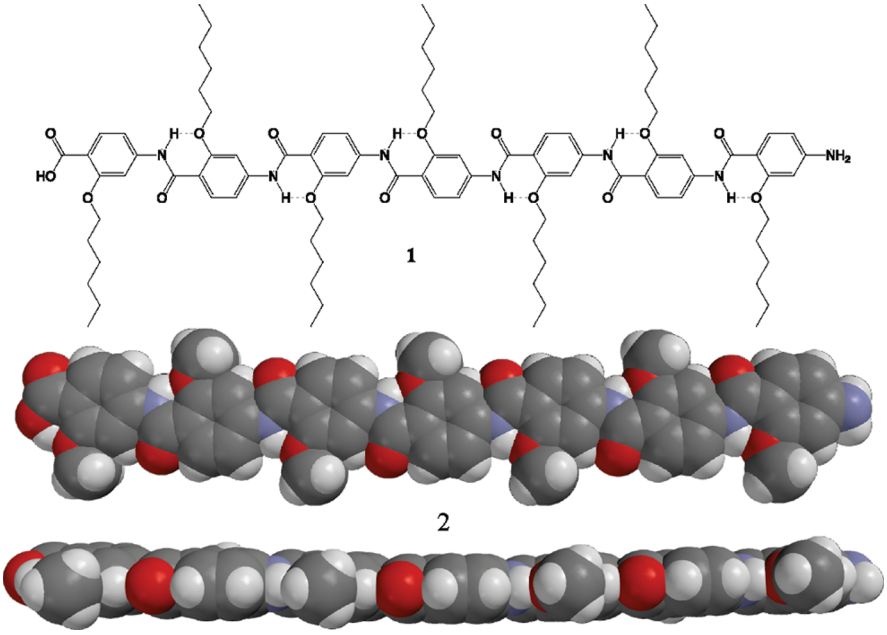


Figure 1. Chemical structure of hepta(2-hexyloxy-*p*-benzamide) (**1**) and calculated (MP2 6-31G*) hepta(2-methoxy-*p*-benzamide) (**2**) in face-on and side-on view.

by Zhang et al. for crescent oligoamides.[18] Detailed studies investigating the mechanism and structure of the aggregation using solid-state NMR techniques are currently under way and will be reported shortly.

This reduction in rotational freedom leads to a highly insoluble material. In order to overcome this solubility problem, our next approach was based on the synthesis of block copolymers composed of monodisperse hairy rod blocks and a highly soluble polymeric segment.

Hairy rods of different oligomerization degrees were prepared on solid support in order to systematically study their solubility characteristics (Scheme 1). Similar to the properties of unsubstituted oligo(*p*-benzamide)s,[14a] the trimeric compound **4a** could be fully characterized in solution. Tri(2-hexyloxy-*p*-benzamide) **4a** was moderately soluble in chloroform/MeOH mixtures and fairly soluble in highly polar aprotic solvents like DMSO. All higher oligomers, including the tetramer **4b** and heptamer **4c**, were insoluble in organic media.

Nonetheless, the synthesis of **4b** and **4c** on solid support proceeded in moderate (46%, **4c**) to good yields (89%, **4b**) as could be determined by the integration of the Fmoc-cleavage elugrams (Figures SI-4 and SI-5, Supporting Information).

As the short *n*-hexyl chain hairs with angstrom length dimensions (~6 Å) were not sufficient to solubilize the stiff aramide backbone, solubilizing poly(ethylene glycol) (PEG) chains were attached to the N-terminus of the oligomeric rods (Scheme 1, bottom) to give polymer conjugates **5b** and **5c**. The long PEG chains with nanometer dimensions (~20 nm for the fully extended chain) and a much larger free volume (compared to the short alkyl chains) can interact better with the solvent. This large interaction volume between solvent and functionalized rods lead to excellent solubility of the conjugated material in good solvents for the PEG chain.[19]

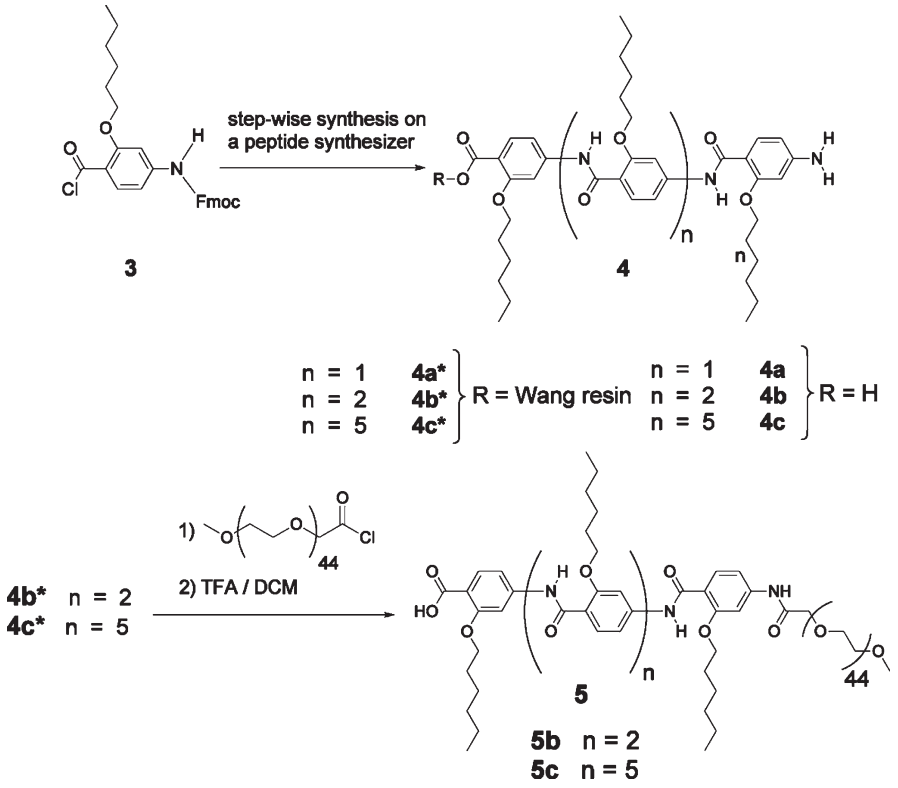
Both PEG conjugates, **5b** and **5c**, which are composed of a tetra(*p*-benzamide) and hepta(*p*-benzamide), respectively, show good solubility in nonpolar organic solvents such as chloroform. Polymer conjugate **5b** could be easily isolated and characterized, as the PEG chain was long enough to prevent the formation of aggregates in chloroform. GPC (Figure 2) and ^{1}H NMR experiments (see Figure SI-3, Supporting Information) showed only the presence of unimers.

On the other hand, characterization of the heptameric PEG conjugate **5c** turned out to be more complicated than expected. Homogenous clear solutions were only obtained for the solvents chloroform and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The analytical GPC trace of the chloroform solution did not show any UV absorbance or refractive index signals. Attempts to characterize the product by ^{1}H NMR spectroscopy gave only broad signals from which the identity of the product could not be unambiguously confirmed (Figure SI-6, Supporting Information). This solution behavior was attributed to the strong aggregation tendency of the copolymer with longer aramide blocks. This trend correlates with previously reported results based on plain aramide−PEG copolymers, where the pentamer was detected as the critical oligoaramide length for aggregate formation in chloroform.[20] Our findings here are also supported by the similar aggregation behavior reported by the groups of Deng and Gong.[18]

Polymer **5c** was additionally characterized qualitatively by IR spectroscopy in the solid state (Figure SI-7, Supporting Information, for sections of the IR-transmission spectra of PEG2000-COOH, model compound poly(2-hexyloxy-*p*-benzamide), and copolymer **5c**). The PEG2000-COOH IR spectrum is dominated by the C−H aliphatic stretch signal at 2881 cm^{-1} and by the C−O stretch signal at 1103 cm^{-1}. The influence of the PEG attachment on the aramide to the product spectrum can be observed by the intensity increase of the C−H vibronic band at 2881 cm^{-1} compared to the next-neighboring signal at higher wavenumbers (see Supporting Information). Comparison of the transmittance ratio Tn_{N-H}/Tn_{C-H} of **1** and **5c** showed a higher value for the copolymer, confirming the overlap of the C−H (PEG) and C−H (alkyl) absorption bands and thereby supporting the assumed product formation. The signal at 1103 cm^{-1} appears also in the copolymer spectrum as a new band arising from the PEG block in the rod−coil polymer (see Supporting Information).

The presence of the PEG absorption bands in the IR spectrum of the copolymer, together with the fact that the product showed good solubility in nonpolar solvents, confirmed the successful attachment of the polymer block to the otherwise insoluble rods. The strong intermolecular interactions in a variety of solvents impeded its detailed characterization and purification. Therefore, the purity level of the crude product could not be determined.

Scheme 1. Synthetic Strategy for the Preparation of Hairy Rod Block Copolymers Consisting of Stiff Oligomeric Benzamide Segments with Pedant Alkyl Groups and a Soluble PEG Block Attached to the N-Terminus of the Oligomer



Dynamic light scattering (DLS) experiments yield a quantitative measure for the fluctuation of scattering particles in solution as characterized by their self-diffusion coefficient and thus their hydrodynamic radius. We therefore performed DLS measurements in order to obtain additional proof for the aggregation and solvent influence on the self-assembly in solution.

DLS measurements of compound **5c** were carried out in chloroform at concentrations varying between 0.1 and 8 g L^{-1}. These measurements confirmed the presence of particles with a large hydrodynamic radius of 279 nm after 1 day of equilibration time. Increasing the equilibration time to 1 week, the hydrodynamic radius obtained for the aggregates increased to 363 nm. Doubling the concentration, afforded supramolecular particles with R_h values of 235 nm within 1 h (see Supporting Information Figures SI-8 and SI-9).

In addition to the measurements in chloroform, **5c** was shown to form high molecular weight aggregates even in HFIP, after 1 h of equilibration time. Despite the high polarity and the ability of HFIP to break hydrogen bonds,[21] the particles reached a hydrodynamic radius of the 94 nm in this solvent (Figure SI-10, Supporting Information). This observation supports our initial assumption that the aggregation of these polymer conjugates is not driven by hydrogen bonds but π-interactions (see above).

To further support this assumptions, we synthesized model trimer **6** (see Supporting Information for details) to investigate the stability of intramolecular hydrogen bond (H_d−O, see Figure 3) in nonpolar (chloroform-*d*) and polar and hydrogen bond breaking solvents (DMSO-d_6). **6** was prepared from 4-amino-2-hexyloxybenzoic acid and 4-aminobenzoic acid using sequence-controlled solid phase synthesis and shows good solubility in both NMR solvents (see Supporting Information). The central phenyl ring of **6** was not hexyloxy-substituted in order to be able to distinguish between the two types of amide N−H protons, i.e., H-bonded and non-H-bonded. ^{1}H NMR spectra of **6** in DMSO-d_6 and chloroform-*d* clearly proved the existence of the intramolecular hydrogen bond (H_d−O, see Figure 3) as seen by the significant downfield shift of the N−H resonance of the H-bonded proton compared to the non-H-bonded proton (H_g, Figure 3). COSY-NMR spectroscopy allowed the assignment of all protons shown in Figure 3 for DMSO-d_6 and chloroform-*d*.

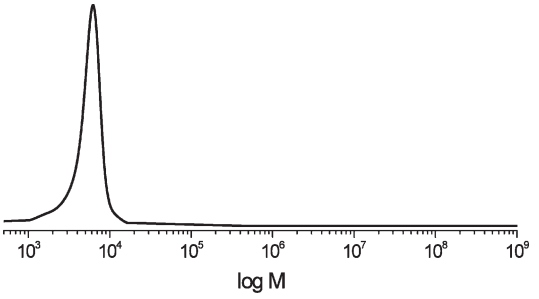


Figure 2. GPC trace of **5b** in chloroform shows only the monomodal distribution of the unimers, without evidence for supramolecular aggregate formation.

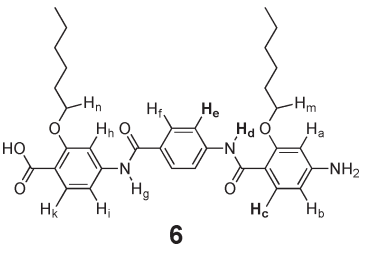


Figure 3. Trimer **6** served as a model for evaluation of the solution conformation. NOE NMR spectroscopy showed the proximity of protons H_e and H_d in chloroform-*d* and DMSO-d_6. Coupling of H_d and H_c could not be detected in either solvent showing the conformational stability of the internal hydrogen bond (H_d−O).

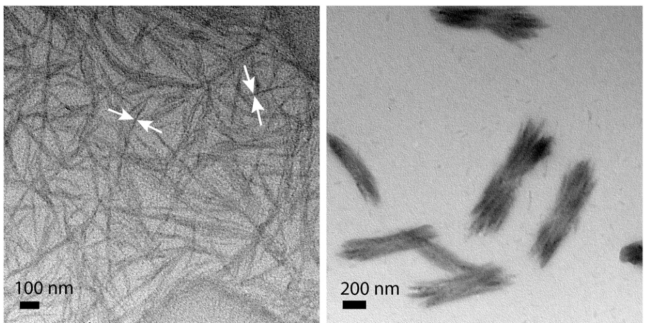


Figure 4. TEM micrographs of **5c**. Drop-cast (three times) from chloroform solution (5 g/L) onto hydrophilized (left) and untreated carbon-coated copper grids (right).

NOE NMR experiments were subsequently carried out to investigate the presence of the H_d-O intramolecular hydrogen bond in both solvents. While the H_d-H_e coupling could be observed in both solvents, H_d-H_c coupling was never detected (see Supporting Information). These experiments support our previous assumption that, similar to the case of the three center hydrogen bonds,[13f] the intramolecular hydrogen bond H_d-O is energetically preferred over a solvent$-H_d$ hydrogen bond. We therefore assume that the intramolecular hydrogen bond is stable in all solvents examined and that aggregation occurs exclusively via π-interactions.

The aggregates of **5c** were further visualized by transmission electron microscopy (TEM) measurements. A chloroform solution of **5c** was drop-cast onto untreated (hydrophobic) as well as freshly O_2-plasma-cleaned (hydrophilic) TEM grid surfaces. Individual fibers with an approximate width of 8 nm are observed, when the TEM grid was treated with an oxygen plasma (Figure 4, left). Deposition of the dissolved aggregates onto the untreated (nonpolar) surface of a TEM grid resulted in the observation of larger bundles of fibers (Figure 4, right). Tapes with a width of ca. 8 nm are most likely formed by π-interactions as the driving force for aggregation. Similar fibers and bundles of fibers were previously observed for poly(*p*-benzamides) carrying triethylene glycol side chains.[15] There, π-interactions were also proposed as the most likely form of aggregation.

Dissolution in the fluorinated solvent HFIP promotes the disruption of these large aggregates to some extent. Shorter and wider noncovalent supramolecular structures (17 nm in width and ~170 nm in length) were visualized via the transmission electron microscope (Figure 5, left).

Although GPC measurements of solutions of **5b** in chloroform demonstrated the absence of aggregates, DLS analysis (see Supporting Information, Figure SI-11) of low concentrated HFIP solutions of **5b** revealed a solvent promoted aggregation even for this shorter oligomeric block. In addition, the TEM micrograph illustrates the stable and extremely rigid morphology of the polymer with a tetramer benzamide block (see Figure 5, right).

As described before, DLS experiments of **5c** solutions in chloroform indicate the formation of supramolecular aggregates, proved by the large hydrodynamic radius. The concentration and equilibration time dependence of the hydrodynamic radius indicate the intermolecular, i.e., noncovalent, origin of the interactions. Chloroform is a good solvent for the PEG polymer as well as the hexyl side chains. Therefore, aggregation is exclusively driven by π-interactions, which are strong enough for superstructure formation in the case of the longer oligomer **5c** but not in the case of tetramer **5b**. HFIP, on the other hand, is a poor solvent for the hexyl side chains giving rise to two types of potential aggregation mechanisms: π-interactions and solvophobic aggregation of the hexyl chains. The particular balance

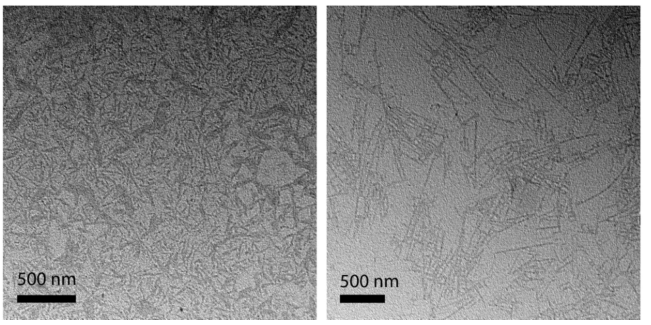


Figure 5. Left: TEM micrograph of **5c**. Drop-cast (three times) from HFIP solution (3 g/L) onto a hydrophilized carbon-coated copper grid. Hydrophilization was performed to avoid agglomeration of the aggregates (as observed in chloroform solution) and for a better adhesion of the solvent on the grid. The rods have monodisperse widths of 17 nm and are ~170 nm long. Right: TEM image of **5b**. Drop-cast (three times) from HFIP ([c] = 5×10^{-2} g/L). The nanorods are monodisperse in width (17 nm) and 240 nm to 1 μm in length.

between these two types of aggregation mechanisms might be the reason for the counterintuitive observation that **5c** forms shorter aggregates in HFIP than **5b**. The TEM observation was also confirmed by DLS measurements of **5b** and **5c** in HFIP (Figures SI-10 and SI-11, Supporting Information).

The very rigid aggregation structures observed for **5b** and **5c** in HFIP resemble those observed for unsubstituted oligo(*p*-benzamide) block copolymers in water reported previously.[17a,22] Although HFIP is applied usually as a hydrogen bond breaking solvent, it is also well-known for its ability to stabilize local hydrogen bonds between close residues in amino acid sequences, particularly in those forming α-helices,[23] but also in some cases facilitating β-sheet formation.[23d] This observation was attributed to the unique properties of HFIP, combining the polar alcoholic and the hydrophobic trifuoromethyl functionalities.[24]

The copolymer **5c** showed an increased aggregation tendency compared to the tetrameric analogue **5b**, making its complete characterization impracticable. **5c** aggregates into long flexible fiberlike structures in chloroform probably due to weak and nondirectional π-interactions. In the solvent HFIP much shorter aggregates are observed possibly due to the dominance of the solvophobic hexyl chain aggregation. For **5b** no aggregation could be observed in chloroform while extremely rigid fibers formed in HFIP. This might be due to a cooperative effect between weak π-interactions reinforced and directionally oriented by neighboring hexyl chain interactions.

Furthermore, it has to be noticed that the characterization of **5c** had to be carried out with the crude product obtained from solid-supported synthesis. On the other hand, only the target sequence was conjugated with the PEG chains due to capping after each monomer addition (see Experimental Part). The deposition of the fiberlike aggregates from nonpolar solutions showed agglomeration into bundles on a hydrophobic surface. This might be due to repulsive interactions of the PEG block with the TEM grid surface and attractive interactions of the alkyl chains with the surface.

Conclusion

We have linked insoluble hairy nanorods of oligo(*p*-benzamide)s to solubilizing PEG chains. The copolymers were soluble and self-assembled in nonpolar (chloroform) and polar (HFIP) solvents. PEG−aramide conjugates with short aramide blocks could easily be purified and characterized in solution. Longer aramide−PEG conjugates aggregated in all solvents examined. Because of the intramolecular saturation of all hydrogen bond donors, we propose a different aggregation mechanism

(π-interactions) for this type of rod−coil block copolymer. Large fiberlike aggregates could be observed in chloroform or HFIP solutions as shown by TEM and DLS experiments.

A well-defined tetra(*p*-benzamide) carrying hexyloxy side chains was shown to form extremely rigid fiberlike aggregates in HFIP, a typical solvent for polyamides. We could show that simple structural alterations in the monomer structure of *p*-aminobenzoic acid (such as the addition of a hexyloxy side chain) can give rise to oligomers with entirely different and enhanced aggregation behavior. This could represent another valuable tool for noncovalent chemistry.

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft (DFG) for funding.

Supporting Information Available: Figures SI-1 to SI-19. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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