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Linear Organo-Soluble Poly(*p*-benzamide)

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ABSTRACT: Organo-soluble, shape-persistent oligo- and poly(*p*-benzamide)s were synthesized and characterized. A triethylene glycol (TEG) substituent was introduced to the *p*-aminobenzoic acid monomer structure as a solubilizing side chain giving 4-amino-2-triethylene glycol benzoic acid. This new monomer was polymerized by the facile polycondensation of the corresponding acid halide derivative of the amine hydrochloric salt. Additionally, a well-defined heptamer was prepared from this monomer on a peptide synthesizer as a model compound. The TEG-substituted oligomers and polymers exhibited good solubility yet high aggregation tendency in common polar and nonpolar organic solvents. The solution self-organization of the poly(2-TEG-*p*-benzamide) was examined by GPC, NMR, and UV/vis spectroscopy. Transmission electron microscopy (TEM) allowed the visualization of the supramolecular assemblies, showing the formation of micrometer-sized rigid superstructures.

Introduction

Aromatic polyamides such as Kevlar and poly(*p*-benzamide) have attracted a great deal of attention due to their inherently extended rigid chain structure. This is caused by the interplay of *para*-linked benzene rings and partial double-bond character of the *trans*-amide linkages.[1] In addition to the rigid chemical structure, the hydrogen-bonding network in aromatic polyamides plays an important role in their thermomechanical properties.[2] The combination of the high persistence length and interchain attraction leads to materials with high mechanical strength and excellent thermal resistance.[3] As a consequence of these features, such polymers are soluble only in a few solvents like DMAc/LiCl and concentrated sulfuric acid, from which fibers can be spin-processed.[3a,4]

Approaches to improve the solubility while maintaining novel material properties of the polyaramides include the introduction of N-protective groups[5] or the synthesis of block copolymers.[6] Another typical strategy to improve solubility in rigid-rod-like molecules is the attachment of flexible side chains to the stiff oligomer/polymer backbone.[7]

Here, we report the facile synthesis of a soluble poly(*p*-benzamide) carrying TEG side chains on the benzene rings. The TEG-grafted polymer and the corresponding oligomeric model compounds are highly interesting materials, as they combine good solubility in common organic solvents with shape persistence and self-organization into supramolecular structures.

Results and Discussion

Synthesis. Monomers were synthesized from 4-aminosalicylic acid as outlined in Scheme 1. 4-Aminosalicylic acid (**1**) was N-acetylated using 1 equiv of acetyl chloride to give **2** in 85% yield. The subsequent reaction with 2-[(methoxyethoxy)ethoxy]ethyl bromide or hexyl bromide produced the corresponding ethers and esters **4a** and **4b** in 75% and 82% yield, respectively. Cleavage of the amide and ester bonds of the TEG- and hexyl-substituted monomers was performed under alkaline conditions to afford amino acids **5a** (70%) and **5b** (85%). *N*-Fluorenylmethyloxycarbonyl (Fmoc) protection of **5a** and **5b** was achieved using 9-fluorenylmethylchloroformate (Fmoc-Cl) to give **8a** and **8b** in moderate to excellent yields (70% and 89%). The activation of the Fmoc-protected amino acids **8a** and **8b** as acid chlorides (**9a** and **9b**), which are needed for subsequent stepwise oligomerizations on solid support, was carried out in situ using $SOCl_2$ and *N*-methylpyrrolidone (NMP).[8]

The free amino acid **5a** was polymerized first in a polycondensation reaction catalyzed by triphenyl phosphite and pyridine in NMP (Scheme 2, path **i**).[9] In a second synthetic pathway the hydrochloride salt of the aromatic amino acid was polymerized upon addition of NMP. Therefore, monomer **5a** was refluxed in $SOCl_2$ to give the corresponding sulfinylaminobenzoyl chloride **6a**.[1] The latter compound was converted to the 2-TEG-4-aminobenzoyl chloride hydrochloride salt **7a** using HCl gas in THF (Scheme 1). After dissolution of **7a** in dry NMP poly(2-TEG-1,4-benzamide) **11aii** was obtained (Scheme 2, path **ii**).

During the polycondensation of the 2-TEG-4-aminobenzoyl chloride **5a** and the corresponding hydrochloride salt **7a**, the afforded polymers remained soluble without the need of adding salts to the solvent. Additionally, the NMP-assisted polycondensation of the ammonium salts achieved a polymer with a stronger aggregation tendency compared to the polycondensation product promoted by triphenyl phosphite, as revealed by the GPC data in polar and nonpolar solvents. According to GPC, polymer **11aii** forms aggregates of higher molecular weight and broader polydispersities than **11ai**, in both DMF and chloroform (see Supporting Information, Table SI 1 and Figure SI 7). Attempts to polymerize the analogous hexyloxy-substituted monomer **5b** using triphenyl phosphite afforded polymer **11bi**, which precipitated from NMP during the polymerization and was only soluble in sulfuric acid (see Supporting Information, Figure SI 3).

Truly monodisperse hepta(2-TEG-1,4-benzamide) and hepta(2-hexyloxy-1,4-benzamide) model compounds were

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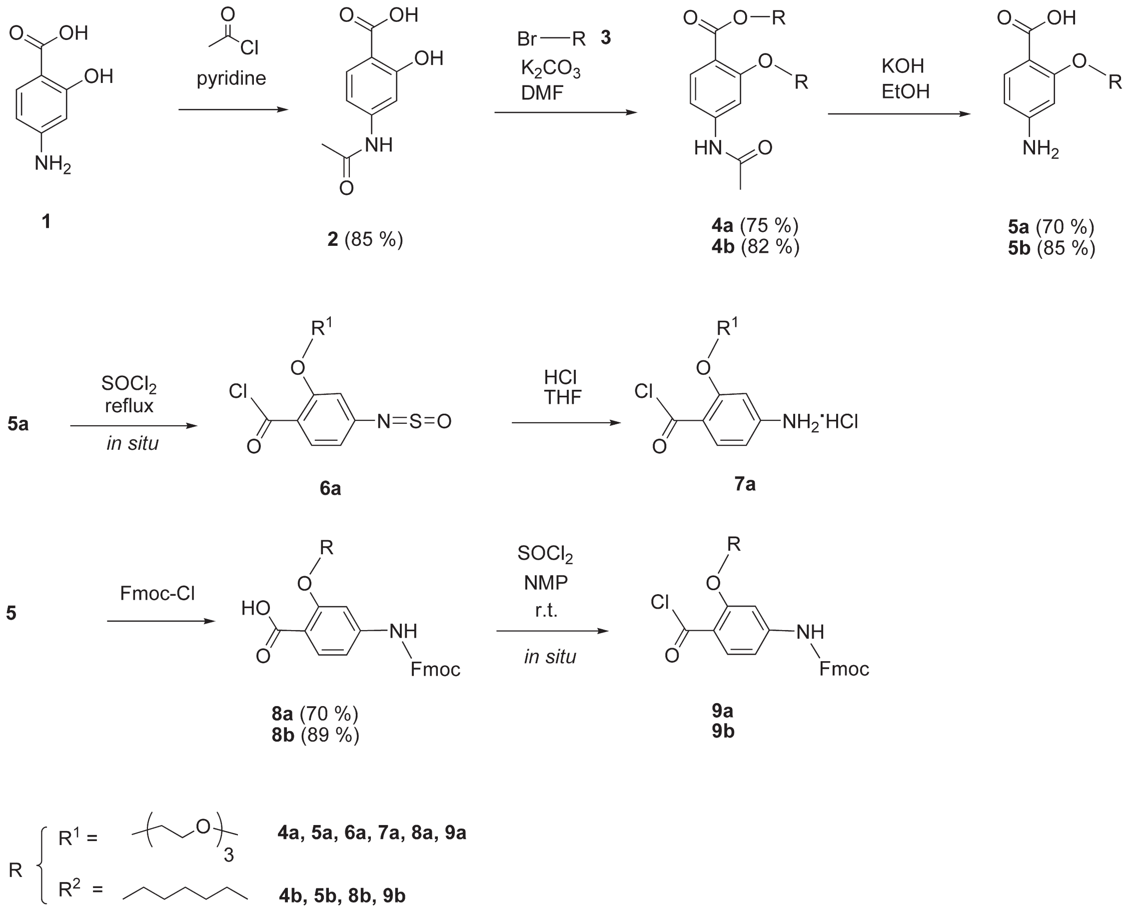
Scheme 1. Synthesis of the Amino Acid Monomers



synthesized on solid support using a commercial peptide synthesizer in analogy to previous reports.[10] Hereby, cycles of *N*-Fmoc deprotection and coupling of **9** were sequentially carried out on the peptide synthesizer,[11] and the final product was cleaved under acidic conditions from the solid support (Scheme 2, path **iii**).

Characterization. Gel permeation chromatography of the TEG-substituted polymer **11aii** in chloroform shows a broad multimodal UV signal over the whole elution volume, suggesting the formation of stable supramolecular aggregates of high molecular weight (see Supporting Information Figure SI 8). As all amide N−H hydrogen bond donors are intramolecularly saturated by the phenyl ether oxygen, it is most likely π-stacking that drives the aggregation. The stability of these aggregated structures is clearly high enough not to be completely disrupted during the elution through a GPC column. Polymer solutions of **11aii** in polar aprotic solvents (DMSO and DMF) revealed the formation of aggregates determined by the signal broadening of the resonance frequencies in the ^{1}H NMR spectrum and the GPC chromatogram (UV detection) (see Supporting Information, Figure SI 8 and Table SI 1). However, the stability of these supramolecular structures is lower than those formed in nonpolar solvents as the molecular weights (determined by GPC in DMF) are noticeably smaller than those observed by GPC in chloroform (see Supporting Information, Figure SI 7).

The photophysical properties of the supramolecular assemblies were investigated via UV/vis spectroscopy. Figure 1 shows the UV/vis absorption spectra of polymer **11aii** and the model heptamer **11aiii** in chloroform. The spectrum of polymer **11aii** shows an hypsochromic shift of the absorption maximum compared to the model heptamer **11aiii** ($\Delta\lambda_{\max}$ = 10 nm). This is attributed to the higher aggregation tendency of the polymer sample. This was also confirmed by ^{1}H NMR analysis in chloroform, where **11aii** shows a significant broadening of the aromatic signals with respect to **11aiii** (see Supporting Information, Figure SI 9). Polymer **11aii** was also investigated by UV/vis spectroscopy in DMSO solution ($\lambda_{\max}$ = 337 nm). Only a small hypsochromic shift was observed compared to its corresponding chloroform solution ($\lambda_{\max}$ = 340 nm) which was attributed to solvent polarity differences. Both polymer **11aii** and heptamer **11aiii**, however, show some degree of aggregation in chloroform-*d* and DMSO-d_6 solution according to ^{1}H NMR spectroscopy. Yet the above UV/vis spectroscopic results do not show the expected blue shift to absorption maxima below 300 nm that were previously observed for aggregating oligo(*p*-benzamide)s.[6c] This might be indicative of a difference in aggregation mechanism due to the presence of the TEG chains in the 2-position and a more extended π-system compared to the nonsubstituted oligomers (see below).

Transmission electron microscopy studies of polymer **11aii** (drop-cast onto carbon-coated copper grids from chloroform solution) show bundles of rigid aggregated superstructures with lengths ranging from nano- to micrometers. These bundles appear to be built from individual fibers that are ~33 ± 6 nm in width.

Many *p*-aromatic polyamides dissolve in selected solvents (usually in tertiary amides) forming anisotropic lyotropic liquid crystalline phases at defined concentrations.[3a,12] The ability of the TEG-grafted poly(*p*-benzamide) **11aii** to form an anisotropic phase in solution was analyzed with an optical microscope using polarized light. Examination of a thin layer of a concentrated solution in DMF showed the birefringence

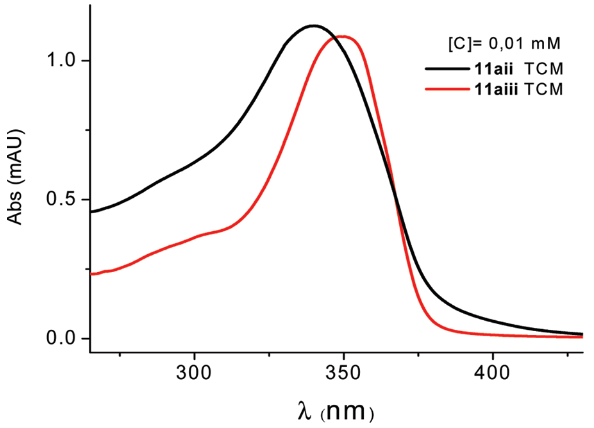
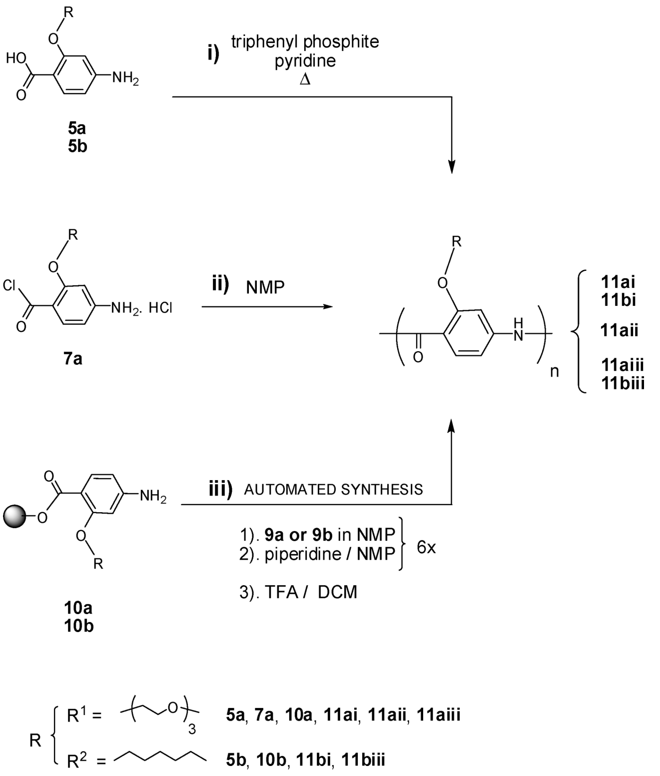


Figure 1. UV absorption spectra of polymer **11aii** and heptamer **11aiii** in chloroform.

Scheme 2. Synthesis of Polydisperse Poly(*p*-benzamide)s (Routes i and ii) and Monodisperse (Route iii) Oligo(*p*-benzamide)s



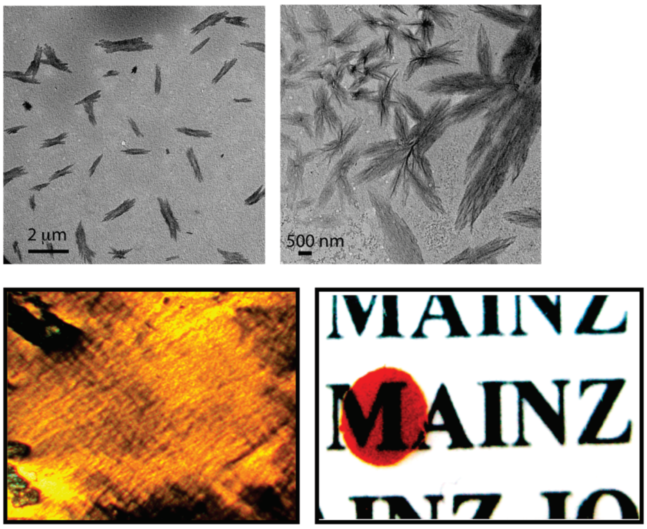


Figure 2. Top: TEM micrographs of **11aii** (drop-cast from chloroform solution [c] = 5 mg/mL, stained with OsO_4). Bottom left: Micrograph (160× magnification) of a solution of **11aii** in DMF ([c] = 87 wt %) under crossed polarizers. Bottom right: Photograph of the same solution of **11aii**.

of the anisotropic phase at room temperature, confirming a highly oriented fluid sample (see Figure 2, [c] = 87 wt % in DMF).

Thermogravimetric analysis (TGA) showed the thermal resistance of the grafted poly(*p*-benzamide)s. The onset decomposition temperatures (T_D) are high for both materials: 394 °C for the insoluble hexyl-grafted polymer and 378 °C for the soluble TEG-grafted polymer (see Supporting Information, Figure SI 10).

Polymers derived from aminosalicylic acid monomers with different side chains, i.e., **11ai**, **11bi**, and **11aii**, showed an enormous solubility dependence on the polarity and chain length of the pendant groups. Hexyl-substituted polymer **11bi** exhibits no solubility in organic media. On the other hand, polymers with TEG side chains (**11ai, 11aii**) showed excellent solubility even in nonpolar solvents. To investigate this phenomenon further, oligomeric model compounds **11aiii** and **11biii** were synthesized in order to evaluate the influence of the side chains on the solubility properties of the oligomer. Both monodisperse heptamers show identical solubility behavior compared to their polymeric analogues. It is known that the introduction of a hydrogen bond acceptor (for example, an ether oxygen) in the *ortho*-position to the carbonyl group of an amide bond induced the restriction of the amide−aryl bond rotation.[13] The *anti*-conformation of the aryl−CO−NH linkages is stabilized by the six-membered hydrogen-bonded ring (see Figure 3a). Because of the conjugation between the amide and aromatic groups, a coplanar or close to coplanar conformation is usually adopted.[13,14] This conformational restriction and coplanar alignment of the adjacent phenyl rings induces a rigid and flat backbone which promotes intermolecular π-stacking. The observed higher UV/vis absorbance maxima compared to previous investigations[6c] also indicate an increased π-overlap and partial conjugation between the phenyl rings across the amide bonds.[15] In addition, the high concentration of nonpolar hexyl side chains on the periphery further reduces the solubility due to side-chain crystallization. Both effects result in lower solubility of the polymer.

The more polar TEG side chains are better solvated and do not tend to crystallize. The longer and more flexible TEG chains may also assume a larger number of conformations in solution; hence, dissolution of the polymer is accompanied by a higher gain in entropy compared to the hexylated oligomers and macromolecules.

We propose that the bundles of fibers observed in Figure 2 (top) are formed via a hierarchical self-organization process. It is feasible that individual polymer chains form π-stacked aggregates coated with TEG side chains. These then form bundles via weaker noncovalent interactions such as van der Waals interactions to yield the observed structures in Figure 2.

Figure 3a shows the *anti*-conformation of the aryl−amide bonds stabilized by hydrogen bond formation and the possible aggregation mechanisms for the fiber formation: (c) π-stacking of individual fibers and (b) the interaction of these aggregates via their TEG coated surfaces.

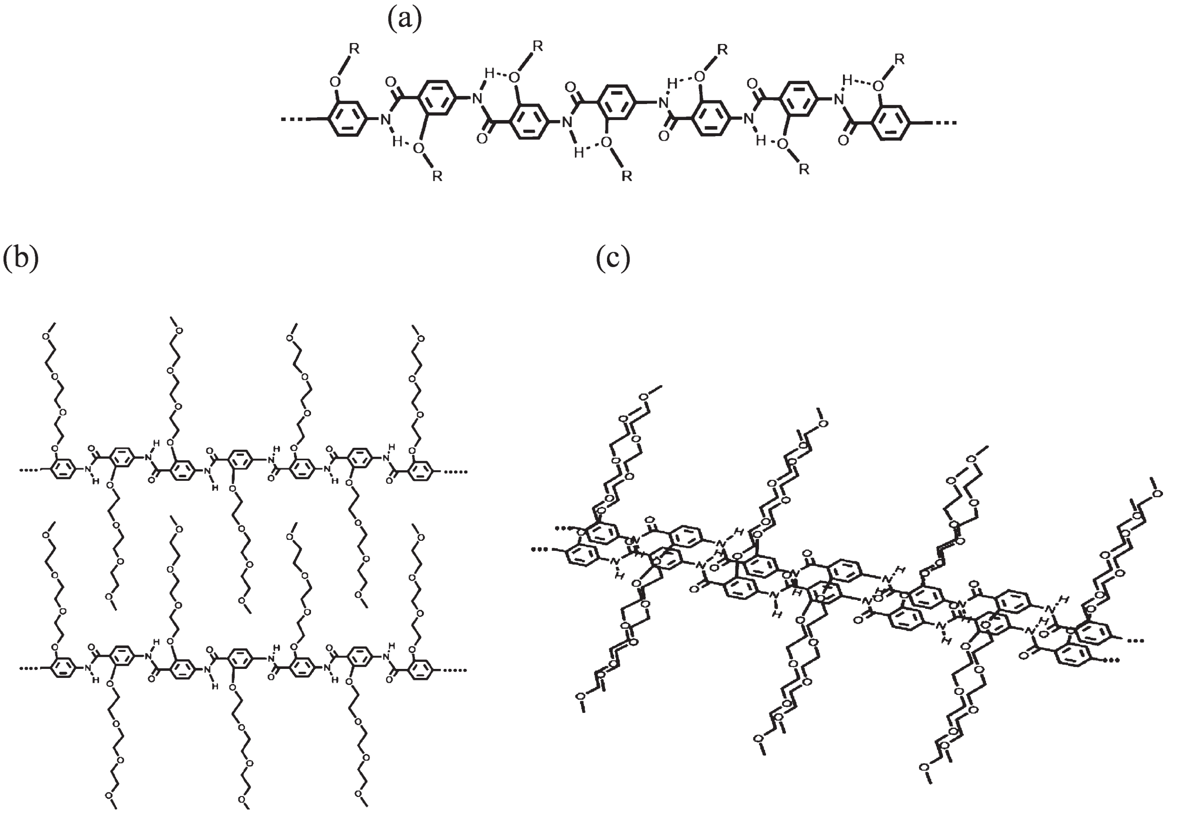


Figure 3. (a) Preferred *anti*-conformation of the aryl−amide bond due to hydrogen-bonded stabilized six-membered ring. Proposed aggregation mechanisms for the fiber formation: (b) van der Waals interactions between TEG chains and (c) π-stacking.

Experimental Details

Materials. NMP was stored over molecular sieves. THF was dried over sodium and distilled under nitrogen prior use. The other reagents and solvents were obtained commercially and used as received. Compound **3** was prepared as described in the literature.[16]

Methods. Nuclear magnetic resonance spectra were recorded on a Bruker AC (300 MHz) or on a Bruker AMX 400 (400 MHz). Infrared spectra were recorded on a Nicolet 5 DXC FT-IR spectrometer. 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 μm). The samples were eluted with an acetonitrile/water gradient (buffered with 0.1% TFA), starting from 10% acetonitrile and rising to 90% over a period of 35 min and maintained constant for an additional 10 min. UV detection was performed at 254 nm. Melting points were recorded on a FP 62 Mettler Toledo in a capillary tube and are uncorrected. Field desorption mass spectra were measured on a Finnigan MAT 95 and ESI mass spectra on a Micromass Q-TOF Ultima 3. Matrix-assisted laser desorption and ionization time of flight (MALDI-ToF) measurements were performed on a Shimadzu Axima CFR MALDI-ToF mass spectrometer equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. 2-(4-Hydroxyphenylazo)benzoic acid (HABA) was used as matrix. UV/vis measurements were accomplished on a V-630 UV/vis spectrophotometer. 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. The synthesis of the monodisperse heptamer was performed on an Applied Biosystems ABI 431a automated peptide synthesizer using standard Fmoc chemistry protocols, similar to the synthesis described before.[16]

Monomer Synthesis. *4-Acetamidosalicylic Acid 2*. Acetyl chloride (23.2 mL, 1 equiv) was added dropwise into a cold solution of 4-aminosalicylic acid **1** (50 g, 0.33 mol, 1 equiv) in pyridine (250 mL) under an inert atmosphere. The solution was further refluxed for 2 h. The cold reaction mixture was poured into a mixture of 800 mL of ice and 400 mL of 6 N hydrochloric acid. The solid was filtered, washed with water, and dried to give **2** (54 g, 85%); mp: 222 °C. ^{1}H NMR: δ (300 MHz, DMSO-d_6) 2.06 (s, 3 H); 7.04 (d, ^{3}J = 8.46 Hz, 1 H); 7.34 (s, 1 H); 7.70 (d, ^{3}J = 8.46 Hz, 1H); 10.21 (s, 1H).^{13}C NMR and DEPT: δ (300 MHz, DMSO-d_6) 24.29 (+); 105.77 (+); 107.48; 110.11 (+); 131.05 (+); 145.7; 162.21; 169.2; 171.69. IR ν (cm^{-1}): 3350, 2872, 1676, 1599, 1535, 1383, 1282, 1222, 1162. RP-HPLC (min): 9.9. M (FD): m/z (%) = 195.6 (100); 196.6 (9.3); 197.6 (0.49); calc [$C_9H_9NO_4$] = 195.1.

4-Acetamido-2-TEG-Benzoic Acid TEG-Ester 4a. **2** (20 g, 0.1 mol), dry DMF (320 mL), TEG-Br **3** (46.4 g, 0.2 mol), 18-crown-6 (0.82 g), anhydrous K_2CO_3 (120 g), and KI were heated for 30 h under reflux and inert atmosphere. The solvent was removed under reduced pressure; water was added to the residue, the resulting solution was extracted with dichloromethane and dried over magnesium sulfate, and the solvent was removed on a rotary evaporator to give **4a** as brown oil (37.3 g, 75%). ^{1}H NMR: δ (300 MHz, $CDCl_3$) 2.16 (s, 3 H); 3.33 (s, 6 H); 3.49−3.83 (m, 20 H); 4.10 (t, 2 H, J = 4.8 Hz); 4.36 (t, 2 H, J = 4.9 Hz); 7.08 (dd, 1 H, ^{4}J = 1.84 Hz, ^{3}J = 8.46 Hz); 7.44 (d, 1 H, ^{4}J = 1.47 Hz); 7.73 (d, 1 H, ^{3}J = 8.46 Hz). ^{13}C NMR and DEPT: δ (300 MHz, DMSO-d_6) 24.37 (+); 58.65 (+); 58.76 (+); 63.36 (−); 68.45 (−); 69.02 (−); 69.21 (−); 69.80 (−); 70.17 (−); 70.32 (−); 70.38 (−); 70.41 (−); 70.57 (−); 71.62 (−); 71.65 (−); 104.27 (+); 110.77 (+); 114.37; 132.54 (+); 143.67; 159.47; 165.14; 169.25. IR ν (cm^{-1}): 3319, 2873, 1693, 1591, 1529, 1406, 1241, 1081, 1025, 847, 776. RP-HPLC (min): 13.6. M (FD): m/z (%) = 526.2 (100); 527.2 (22); 528.2 (5.6); calc [$C_{23}H_{37}NO_{10}K$] = 526.2.

4-Acetamido-2-hexyloxybenzoic Acid Hexyl Ester 4b. The reaction was performed as described for **4a**. **2** (37.1 g, 0.19 mol), dry DMF (700 mL), 1-bromohexane (153 mL, 1.1 mol), 18-crown-6 (1,5 g), anhydrous K_2CO_3 (229.8 g), and KI were heated for 50 h under reflux and inert atmosphere. After removal of the dichloromethane, the residue was cooled overnight at −18 °C; the precipitate was collected by suction filtration, washed with cold petroleum, and dried in vacuum to give **4b** as a beige solid (56.7 g, 82%); mp: 66 °C. ^{1}H NMR: δ (300 MHz, DMSO-d_6) 0.84−0.89 (m, 6 H); 1.25−1.49 (m, 12 H); 1.59−1.76 (m, 4 H); 2.06 (s, 3H); 3.94 (t, ^3J = 6.25 Hz, 2 H); 4.15 (t, ^3J = 6.4 Hz, 2 H); 7.16 (dd, ^4J = 1.7 Hz, ^3J = 8.6 Hz, 1 H); 7.47 (d, ^4J = 1.47 Hz, 1 H); 7.64 (d, ^3J = 8.46 Hz, 1 H); 10.18 (s, 1 H). ^{13}C NMR and DEPT: δ (300 MHz, DMSO-d_6) 13.87 (+); 22.08 (+); 22.14 (+); 24.2 (+); 25.21 (−); 25.3 (−); 28.31 (−); 28.68 (−); 31.03 (−); 31.08 (−). IR ν (cm^{-1}): 3306, 3272, 2955, 2932, 2856, 1679, 1662, 1595, 1543, 1409, 1274, 1261, 1191, 1138, 831. RP-HPLC (min): 35.6. M (FD): *m*/*z* (%) = 363.4 (100); 364.4 (19); calc $[C_{21}H_{33}NO_4]$ = 363.2.

*4-Amino-2-TEG-Benzoic Acid **5a***. A solution of **4a** (14.17 g, 0.029 mol), KOH (6.8 g), and ethanol (100 mL) was heated under reflux for 50 h. The solvent was then removed under reduced pressure; the residue was dissolved in water and extracted with chloroform. The aqueous phase was then neutralized and extracted, and the product was isolated by concentration of the organic phase. Chromatographic purification (eluent chloroform:MeOH 15:1) afforded the pure product **5a** (6 g, 70%). ^{1}H NMR: δ (300 MHz, DMSO-d_6) 3.36 (s, 3 H); 3.52−3.55 (m, 2 H); 3.63−3.73 (m, 6 H); 3.88 (t, ^3J = 4.6 Hz, 2 H); 4.27 (t, ^3J = 4.6 Hz, 2 H); 6.22 (d, ^4J = 1.84 Hz, 1 H); 6.35 (dd, ^3J = 8.46 Hz, ^4J = 2.21 Hz, 1 H); 7.91 (d, ^3J = 8.46 Hz, 1 H). ^{13}C NMR and DEPT: δ (300 MHz, DMSO-d_6): 58.74; 68.48 (−); 68.54 (−); 70.29 (−); 70.33 (−); 70.45 (−); 71.64 (−); 97.82 (+); 106.64; 108.4 (+); 134.9 (+); 153.5; 159.15; 166.15. IR ν (cm^{-1}): 3446, 3354, 3235, 2877, 1701, 1600, 1449, 1336, 1268, 1196, 1095, 1035, 832. RP-HPLC (min): 9.1. M (FD): *m*/*z* (%) = 322.12 (100); 323.13 (4); calc $[C_{14}H_{21}NO_6Na]$ = 322.1.

*4-Amino-2-hexyloxybenzoic Acid **5b***. A solution of **4b** (55.3 g, 0.15 mol), KOH (35 g) and ethanol (550 mL) were heated under reflux for 50 h. The solvent was then removed under reduced pressure, the residue dissolved in water (550 mL) and neutralized with 6 N HCl. The precipitate was collected, washed well with water and dried under vacuum at 60 °C to give **5b** (30.3 g, 85%); mp: 122 °C. ^{1}H NMR: δ (300 MHz, DMSO-d_6) 0.87 (t, ^3J = 6.99 Hz, 3 H); 1.26−1.31 (m, 4 H); 1.43 (m, 2 H); 1.71 (tt, 2 H); 3.93 (t, ^3J = 6.4 Hz, 2 H); 5.86 (s, 2H); 6.14 (dd, ^4J = 1.84 Hz, ^3J = 8.46 Hz, 1 H); 6.2 (d, ^4J = 2.21 Hz, 1 H); 7.50 (d, ^3J = 8.82 Hz, 1 H); 11.31 (s, 1 H). ^{13}C NMR and DEPT: δ (300 MHz, DMSO-d_6) 13.88 (+); 22.08 (−); 25.09 (−); 28.58 (−); 30.94 (−); 67.98 (−); 97.22 (+); 105.82 (+); 106.06; 133.79 (+); 154.49; 160.42; 166.34. IR ν (cm^{-1}): 3428, 3345, 3232, 2930, 1685, 1586, 1456, 1401, 1339, 1267, 1191, 998, 831. RP-HPLC (min): 21.9 min. M (FD): *m*/*z* (%) = 237.8 (100); 238.8 (17); 239.8 (1.4); calc $[C_{13}H_{19}NO_3]$ = 237.1.

*N-Fmoc-4-amino-2-TEG Benzoic Acid **8a***. **5a** (5.67 g, 19 mmol) was dissolved in dry NMP (30 mL) under an inert atmosphere followed by the dropwise addition of Fmoc-Cl (5.39 g, 21 mmol) in dry NMP (15 mL). After 24 h, the reaction mixture was poured slowly into 300 mL of water. The beige precipitate was collected by filtration, washed with water, and recrystallized twice from toluene to afford **8a** (6.7 g, 13 mmol, 70%); mp: 126 °C. ^{1}H NMR: δ (300 MHz, DMSO-d_6) 3.28 (s, 3 H); 3.43−3.46 (m, 2 H); 3.51−3.64 (m, 6 H); 3.81 (t, ^3J = 4.41 Hz, 2 H); 4.22−4.29 (m, 3 H); 4.63 (d, ^3J = 6.25 Hz, 2 H); 6.83 (dd, ^3J = 8.6 Hz, ^4J = 1.7 Hz, 1 H); 7.33 (t, ^3J = 7.35 Hz, 2 H); 7.42 (t, ^3J = 7.2 Hz, 2 H); 7.5 (s, 1 H); 7.56 (s, 1 H); 7.64 (d, ^3J = 6.99 Hz, 2 H); 7.79 (d, ^3J = 7.35 Hz, 2 H); 8.03 (d, ^3J = 8.82 Hz, 2 H). ^{13}C NMR and DEPT: δ (300 MHz, DMSO-d_6) 46.56 (+); 58.02 (+); 65.83 (−); 68.39 (−); 68.6 (−); 69.59 (−); 69.85 (−); 70.11 (−); 71.26 (−); 103.05 (+); 109.83 (+); 114.49; 120.22 (+); 125.12 (+); 127.16 (+); 127.74 (+); 132.46 (+); 140.83; 143.69; 143.96; 153.24; 158.72; 166.37. IR ν (cm^{-1}): 3270, 2900, 1728, 1593, 1536, 1428, 1218, 1193, 1132, 1084, 1063, 1045, 1002, 858, 842, 745. RP-HPLC (min): 25.9. M (FD): *m*/*z* (%) = 544.2 (100); 545.2 (24.9); 546.2 (1.4); calc $[C_{29}H_{31}NO_8Na]$ = 544.2.

*N-Fmoc-4-amino-2-hexyloxybenzoic Acid **8b***. **5b** (19.9 g, 84 mmol) was dissolved in dry NMP (140 mL) under an inert atmosphere followed by the dropwise addition of Fmoc-Cl (21.67 g, 83.8 mmol) in dry NMP (55 mL). After 24 h, the reaction mixture was poured slowly into 280 mL water. The beige precipitate was collected by filtration, washed with water, petroleum ether and recrystallized from toluene to afford **8b** (38.6 g, 89%); mp: 159 °C. ^{1}H NMR: δ (300 MHz, DMSO-d_6) 0.86 (t, ^3J = 6.62 Hz, 3 H); 1.27−1.30 (m, 4 H); 1.43 (m, 2 H); 1.71 (tt, 2 H); 3.95 (t, ^3J = 6.25 Hz, 2 H); 4.32 (t, ^3J = 6.62 Hz, 1 H); 4.52 (d, ^3J = 6.62 Hz, 2 H); 7.08 (d, ^3J = 8.09 Hz, 1H); 7.33−7.45 (m, 5 H); 7.65 (d, ^3J = 8.46 Hz, 1H); 7.76 (d, ^3J = 6.99 Hz, 2 H); 7.91 (d, ^3J = 7.35 Hz, 2 H), 9.98 (s, 1H). ^{13}C NMR and DEPT: δ (300 MHz, DMSO-d_6) 13.87 (+); 22.06 (−); 25.01 (−); 28.5 (−); 30.9 (−); 46.56 (+); 65.8 (−); 68.15 (−); 102.63 (+); 109.34 (+); 114.43; 120.19 (+); 125.11 (+); 127.13 (+); 127.71 (+); 132.34 (+); 140.82; 143.69; 143.87; 153.24; 158.94; 166.57. IR ν (cm^{-1}): 3302, 3218, 2952, 2932, 2856, 1738, 1710, 1608, 1528, 1414, 1309, 1196, 1103, 736. RP-HPLC (min): 34.9. M (FD): *m*/*z* (%) = 459.5 (100); 460.6 (16.7); calc $[C_{28}H_{29}NO_5]$ = 459.2.

Polycondensation. *Polycondensation Method **i** Using Triphenyl Phosphite*. A mixture of monomer (**5a**, **5b**) (3.3 mmol), triphenyl phosphite (3.3 mmol), NMP or dichlorobenzene (6.6 mL), and pyridine (1.65 mL) was heated under argon at 100 °C (for NMP) or at 80 °C (for dichlorobenzene). After 6 h methanol was added, and the precipitate was filtered, washed well with methanol, water, again with methanol, and then with diethyl ether. Polymer (**11ai**, **11bi**) precipitated from the reaction mixture after 3 h, affording a product insoluble in methanol, chloroform, DMSO, DMF, DMF/LiBr, NMP, or hexafluorobenzene.

11ai *^{1}H NMR*. δ (400 MHz, D_2SO_4) 3.77−4.7 (m, 15 H); 7.31−8.62 (m, 3 H). IR ν (cm^{-1}): 3334, 2922, 2871, 1668, 1582, 1502, 1454, 1411, 1230, 1095, 848.

11bi: *^{1}H NMR*. δ (400 MHz, D_2SO_4) 0.42 (br. s, 3 H), 0.89−1.03 (m, 6 H), 1.55 (br. s, 2 H), 4.05 (br. s, 2 H), 6.67−7.91 (m, 3 H). IR ν (cm^{-1}): 3339, 2928, 2857, 1669, 1581, 1517, 1409, 1236, 1191, 1121, 1018, 760.

*Polycondensation Method **ii** of Sulfinylamino-2-TEG Benzoyl Chloride*[1]. 4-Amino-2-TEG-benzoic acid **5a** (1.36 g, 4.5 mmol) was refluxed in thionyl chloride (30 mL). After 3 h, the excess of thionyl chloride was removed overnight under vacuum to afford *p*-sulfinylamino-2-TEG benzoyl chloride **6**. After dissolution in dry THF (60 mL), the solution was cooled with an external ice bath and HCl was passed through for 2.5 h. The solvent was removed under reduced pressure; dry NMP (20 mL) was added, and stirring was continued at room temperature. After 3 days the product was precipitated in MeOH, centrifugated, and washed with water (2×) to obtain **11aii** (0.63 g, 46%).

Heptamer Synthesis. *Resin Functionalization*. Wang resin (417 mg, 0.25 mmol, loading: 0.6 mmol/g) was swollen in a minimum amount of dry NMP. Fmoc-protected amino acid **8a** or **8b** (2 mmol) was dissolved in NMP (2 mL), and thionyl chloride (0.22 mL, 3 mmol) was added. After 2 h, the solution was evacuated for 30 min and poured to the Wang resin. After 24 h the resin was drained and washed four times with NMP. Unreacted functional groups on the resin were capped with a solution of 4-nitrobenzoyl chloride (0.46 g, 2.5 mmol) in NMP (1.5 mL).

*Preparation of the Acid Chloride **9a** and **9b** for the Automated Solid-Phase Synthesis*. **8a** or **8b** (13 mmol) was dissolved in thionyl chloride (30 mL), and a catalytic amount of dry NMP was added. After stirring for 2.5 h, thionyl chloride was removed under reduced pressure, the acid chloride was redissolved in dry DCM, and the solvent was removed again under vacuum. Dry NMP (23.5 mL) was added, and the solution was filtered through a 400 μm syringe filter into the cartridges of the peptide synthesizer (1 mmol per cartridge).

*Automated Heptamer (**iii**) Synthesis on a Peptide Synthesizer*. The functionalized resin was N-deprotected and reacted with 4 equiv of acid chloride **9a** or **9b** (2×), followed by the reaction with 4 equiv of 4-nitrobenzoyl chloride as capping reagent (0.54 mmol/mL, 2 mL). This sequence was repeated six times to afford the heptamer **11aiii** or **11biii**. The efficiency of the monomer coupling steps was monitored during the synthesis by UV detection of the deprotected Fmoc groups. The oligomer was cleaved off the solid support by stirring in TFA-DCM (50%) solution for 12 h.

11aiii. The solvent was concentrated, and the crude product was precipitated in ether and centrifugated (0.39 g, 0.2 mmol, 80%). Purification by column chromatography (1/0.1 chloroform/MeOH) afforded 180 mg of pure product. ^{1}H NMR: δ (400 MHz, DMSO-d_6) 3.15−3.23 (m, 21 H); 3.3−4.1 (m, 70 H); 4.13−4.4 (m, 14 H); 6.27 (m, 2 H); 7.20−7.42 (m, 6 H); 7.6−7.97 (m, 13 H); 10.18−10.41 (m, 6 H).

11biii. The solvent was concentrated, poured into ether, and centrifugated to afford a product insoluble in organic solvents.

Conclusions

A new soluble poly(*p*-benzamide) with triethylene glycol side chains was developed. The high solubility in organic solvents, in addition to the shape persistence and thermal stability, shows great promise for this material, where tedious processing using sulfuric acid could be replaced by an ordinary solvent. To the best of our knowledge, this is the first example of such a linear polymer that can be processed from organic media. The polymers self-assemble into fiber-like structures which for higher ordered hierarchical superstructures. Bundles of fibers can be observed via TEM but do not allow a molecular correlation. Concentrated solutions of the polymeric materials in DMF yielded anisotropic fluids, i.e., exhibited lytropic liquid crystallinity.

The synthesis developed here will open the door to other substituted rigid-rod-like polymers based on polyamides. As polyamides are typically more straightforward in their synthesis compared to many other polycondensation polymers, they have the potential to replace other aromatic rigid-rod-like structures such as for example poly(*p*-phenylene)s in matters where ease of synthesis and shape persistence are concerned.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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