Rod−Coil and Coil−Rod−Coil Block Copolymers with Oligo(*p*-phenyleneethynylene) as the Rod Block

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Introduction. Block copolymers reveal a wide variety of phases and, therefore, appear to be ideal candidates for the development of new functional materials.[1] Recently block copolymers consisting of flexible and rodlike blocks have attracted much attention.[2−7] Examples for such rod−coil block copolymers are poly(γ-benzyl glutamate-*b*-butadiene),[3] poly(*p*-phenylenevinylene-*b*-norbonene),[4] poly(*p*-phenylene-*b*-styrene),[5] poly(hexyl isocyanate-*b*-styrene),[6] and polyisoprene or poly(isoprene-*b*-styrene) with a liquid crystalline mesogen at the chain end.[7] Especially the work of Stupp[7] and of Ober and Thomas[6] proves which fascinating and surprising supramolecular arrangements are taken by such rod−coil block copolymers. Our curiosity is directed towards rod−coil block copolymers with oligo(*p*-*p*henyleneethynylene) (oligoPPE) as the rod block. PolyPPE is of interest due to its electro- and photoluminescence.[8] These optical characteristics are influenced by intermolecular interaction,[8b,9] and therefore the morphology of the material.[10] It appears interesting to investigate the type and degree of ordering of the oligoPPE unit as part of a block copolymer and the effect of this ordering on the optical characteristics. Furthermore, attaching flexible polymers to the ends of oligoPPE may be advantageous for the processing of luminescent devices with oligoPPE as the active component.

In this communication we report on the synthesis of the rod−coil diblock copolymer poly(PPE-*b*-1,4-isoprene) and its subsequent transformation into a coil−rod−coil triblock copolymer. The latter architecture is well-known for liquid crystalline compounds of low molecular weight. On polymeric analogues, however, only theoretical considerations[11] have been published up to now.[12]

Results and Discussion. Because the formation of supramolecular assemblies is sensitive to molecular heterogeneities such as polydispersity, to us it appears important to investigate a synthetic route to narrowly distributed samples. Recently, we have developed a facile route to monodisperse oligoPPE, which was pursued up to a nonamer.[13,14] To test our strategy for the synthesis of rod−coil block copolymers with PPE units, we used the rather short acid **1** as the rod block (Scheme 1). Acid **1** is a bifunctional rodlike molecule with a carboxylic acid end group and a silyl-protected terminal ethyne group. As the coil block we chose narrowly distributed 2-(poly-1,4-isoprenyl)ethanol (PIOH; polydispersity = 1.05), which consisted mainly of repeat units formed by 1,4-addition. It had been produced by anionic polymerization of isoprene in cyclohexane and quenching with ethylene oxide. Acid **1** and PIOH were linked via an ester formation according to the protocol of Mitsunobu[15] giving the rod−coil diblock copolymer **2**. Some of acid **1** remained unreacted, although PIOH had been used in excess. The reason for this is not yet understood. Luckily, **1** was easily removed by filtration of the crude product through a short silica gel column. After desilylation of **2**, the terminal acetylene group of **3** can be used for further transformations. Copper-catalyzed oxidative acetylene dimerization in pyridine

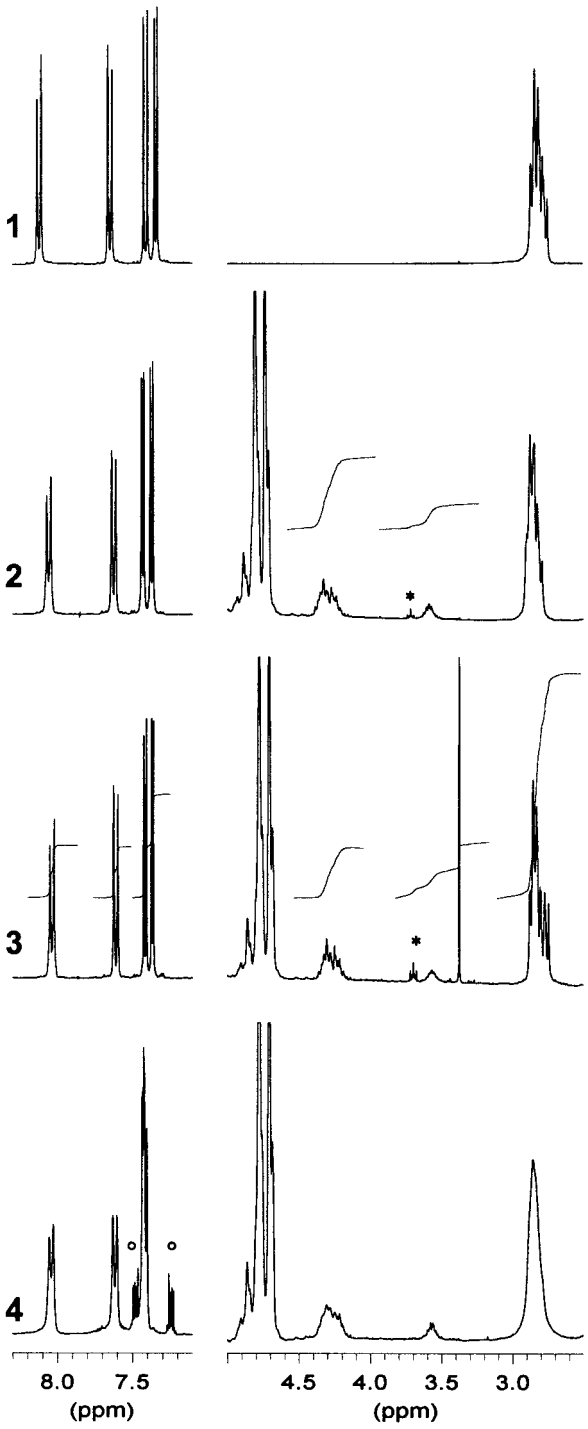

Figure 1. ^{1}H NMR spectra (CD_2Cl_2, 300 MHz, room temperature) of acid **1** and block copolymers **2**−**4**: (*) THF; (○) 1,2-dichlorobenzene.

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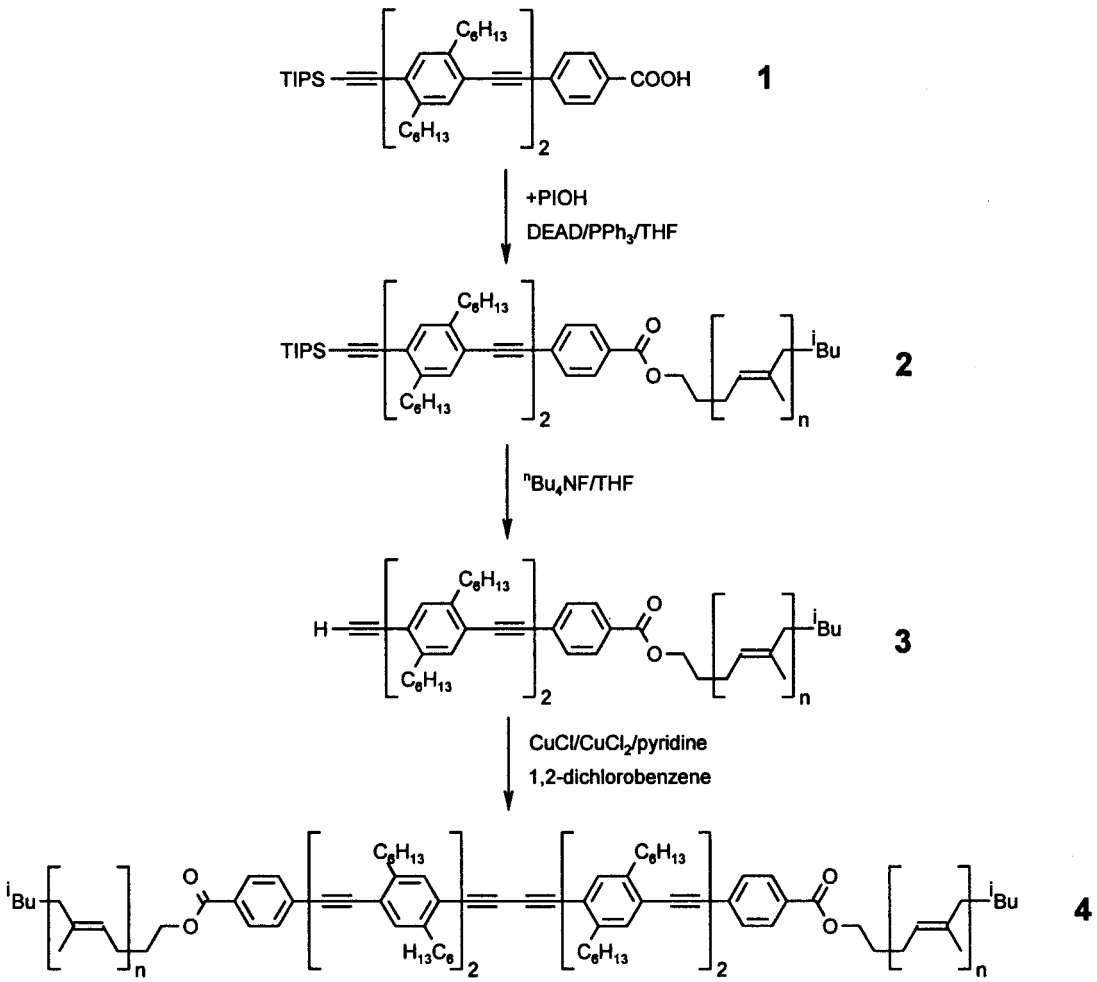
Scheme 1[a]



[a] Key: DEAD = diethyl azodicarboxylate. For reasons of clarity, only the 1,4-constitution of PIOH and one of the two possible double bond configurations is shown in the scheme.

and 1,2-dichlorobenzene gave the coil−rod−coil triblock copolymer **4**. Addition of 1,2-dichlorobenzene as a cosolvent was necessary due to the low solubility of **3** in pyridine.

The proposed molecular structures of the block copolymers were proven by high-resolution NMR spectroscopy (Figure 1). The ^{1}H NMR spectrum of **2** shows, besides the dominant signals of the polyisoprene repeating units, the characteristic signals of the rod part, i.e., the signal pattern of an AA′BB′ spin system and four singlets in the aromatic region caused by the carboxyl and the dihexyl-substituted aromatic rings, repectively, and a multiplet around 2.8 ppm corresponding to the benzylic protons. Comparing the ^{1}H NMR spectra of starting material **1** and of copolymer **2**, the aromatic protons in the ortho position to the carboxyl group are found to be shifted slightly to higher field by the esterification of acid **1**. This is consistent with the observation that these protons experience a slight downfield shift when acid **1** is prepared by hydrolysis of the corresponding methyl ester. Another informative signal belongs to the oxymethylene protons of the PIOH block. These protons cause a multiplet that is shifted from 3.6 to 4.3 ppm on transformation of PIOH into **2**. The latter value is typical for an oxymethylene group of an ester. By integration of these multiplets, the degree of derivatization of PIOH was determined to be ca. 80%. Desilylation of **2** afforded a new singlet at 3.38 ppm, a value characteristic of the acetylenic protons of oligoPPEs.[13] After dimerization of **3**, this signal is no longer present. All proton signals of the rod block of **4** are broadened in comparison to those of **3**. Additionally, the aromatic protons of the dihexyl-substituted benzene rings were shifted distinctly on dimerization.

The ^{13}C NMR spectra (see Supporting Information) are in agreement with the structures of **2**−**4**. The signals for the carboxyl group of **2**−**4** appear at 166 ppm, i.e., as expected at higher field than the corresponding signal of acid **1** at 171 ppm.[16] Very informative signals originate from the acetylenic carbons. The four signals of the diaryl-substituted acetylenes appear in the range of 92−94 ppm. Two additional signals of the silylated ethyne group of **2** appear at 106 and 96 ppm. Instead of these signals, the carbon spectrum of **3** shows two signals at 83 and 82 ppm for the monosubstituted ethyne group. On formation of the 1,4-diarylbutadiyne structure of **4**, these signals are replaced by signals at 82 and 79 ppm. This is in accordance with the proposed diyne structure. A pair of signals at 82 and 79 ppm had been found to be characteristic of a diarylbutadiyne moiety for the PPE-system used in this work.[12,17]

Size exclusion chromatography (SEC; universal calibration with polystyrene standards) is particularly instructive (Figure 2). While PIOH is traceable by a refractive index (RI) detector but not by a UV detector, copolymers **2**−**4** are detectable by both. This offers an easy proof of whether the binding of the rod to the coil had been successful. RI and UV detection of **2** gave

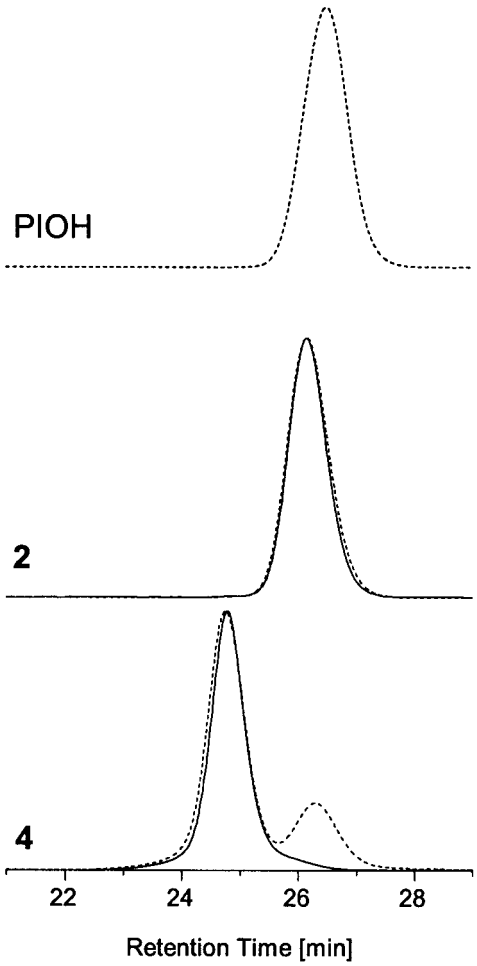


Figure 2. SEC eluograms (THF, room temperature, RI detection: ---, UV-detection: —) of PIOH and of block copolymers **2** and **4**.

nearly identical SEC traces. The rod is about 21 Å long, and attaching it to the PIOH coil evokes a clear increase in the hydrodynamic volume: For the starting material PIOH, M_n was calculated to be 6496. For **2** a molecular weight of 6999 was determined. Dimerization of **3** results in approximately a doubling of the molecular weight (M_n = 12 960). While the SEC trace of **4** obtained with UV detection shows a monomodal distribution, the SEC trace obtained with RI detection clearly reveals residual PIOH that had not been derivatized with acid **1**, as was suggested by ^{1}H NMR spectroscopy. The difference in molecular weight of PIOH and copolymer **4** should be sufficient to allow separation of PIOH and **4** by preparative SEC.

The successful synthesis of the narrowly distributed rod−coil diblock copolymer **2** and the coil−rod−coil triblock copolymer **4** is a sound basis for further syntheses with longer PPE derivatives such as the available tetramer or nonamer,[13,14] and other flexible polymers, e.g., polystyreneethanol. Optimization of the esterification step, experiments to separate unreacted PIOH from **2** and **4**, and thermal and optical characterization of the new materials are under investigation.

Experimental Part. Formation of Copolymer 2. The solutions of PIOH (1.70 g, ≈0.26 mmol; M_n = 6496, M_w = 6815) in dry THF (10 mL) and of acid **1** (0.20 g, 0.24 mmol) in dry THF (10 mL) were combined. After degassing the mixture by a freeze−pump−thaw cycle, triphenylphosphine (0.076 g, 0.289 mmol) and diethyl azodicarboxylate (0.05 mL, 0.32 mmol) were added successively. The reaction mixture was stirred at room temperature for 3 days. Addition of triphenylphosphine (0.076 g) and diethyl azodicarboxylate (0.05 mL) was repeated, and the mixture was stirred for another 3 days. Then the solvent was rotated off and the residue was filtered through silica gel (silica gel 60 with 230−400 mesh purchased from Fluka; dichloromethane/petroleum ether (30−40 °C) 2:1 v/v) in order to remove unreacted acid **1** that remains on the column at the starting point. Diblock copolymer **2** (1.2 g, ≈66%), containing ca. 20% of PIOH, was obtained as a colorless, turbid oil.

Desilylation of Copolymer 2. To a solution of **2** (0.62 g, ≈0.08 mmol) in THF (20 mL) was added tetrabutylammonium fluoride (0.08 mL, 1.0 M in THF), and the solution was stirred for 2 h at room temperature. After addition of water (20 mL), THF was rotated off. The residual watery phase was extracted with CH_2Cl_2 (3 × 20 mL). After drying ($MgSO_4$), the solvent was removed in vacuo, giving **3** (0.54 g, ≈93%) as a pale yellow, fluorescent, turbid oil.

Dimerization of Copolymer 3. $CuCl_2$ (22 mg, 0.16 mmol) and CuCl (8 mg, 0.08 mmol) were suspended in dry pyridine (20 mL) at 0 °C. The ice bath was removed, and **3** (0.294 g, ≈0.041 mmol), dissolved in 1,2-dichlorobenzene (20 mL), was added. The reaction mixture was degassed and stirred at room temperature for 3 days. After addition of CH_2Cl_2 (20 mL), the reaction mixture was washed with 2 N HCl (3 × 30 mL) and finally with water and was dried ($MgSO_4$). The solvents were removed in vacuo, yielding triblock copolymer **4** (0.20 g, ≈68%), as a yellow, fluorescent, very viscous oil contaminated with ca. 20% of PIOH.

Supporting Information Available: ^{13}C NMR spectra of acid **1**, of block copolymers **2**−**4**, and a butadiyne model compound (6 pages). Ordering information is given on any current masthead page.

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(17) For comparison, the ^{13}C NMR spectrum of a butadiyne model compound has been included in the Supporting Information.

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