



Stimuli-responsive coil-rod-coil block copolymers synthesized by using a bis-alkoxyamine-functionalized poly(*para*-phenylene) macro initiator



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ABSTRACT

The preparation of coil-rod-coil block copolymers possessing a rigid poly(*para*-phenylene) middle segment surrounded by either temperature- or pH-responsive blocks is described. First, the bis-alkoxyamine terminated macro initiator was synthesized using microwave-accelerated Suzuki polycondensation (SPC). Afterwards the macro initiator was applied for the nitroxide-mediated radical polymerization (NMRP) of N-isopropyl acrylamide (NIPAAm) and 2-vinyl pyridine (2VP), respectively, to attach defined thermo- or pH-sensitive blocks. Macro initiator and block copolymer molecular weight and molecular weight distribution determinations were conducted via size exclusion chromatography (SEC). In addition ¹H NMR spectroscopy was used to determine block ratios and molecular weights complementary. Further block copolymer characterization was performed by DSC, AFM, SEM measurements as well as turbidity and titration experiments. Critical transition values were found to be little different than for respective homo polymers.

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1. Introduction

Responsive polymers are able to react to changes in environmental conditions. Such stimuli are typically subdivided into physical, chemical and biological effects [1]. Strikingly already small changes in environmental conditions can evoke a large response of the polymers. Such response can be seen in changes in shape, dimension, permeability, and wetting as well as changes in optical, mechanical, and electrical properties [2–4]. Hence, a variety of applications have been reported such as drug delivery [5–7], biotechnological systems [8], micro valves [9–11], switchable surfaces [12], sensors and actuators [13] as well as stationary phases in chromatography [14].

Special attention has been paid to block copolymers with at least one stimuli-responsive block. Block copolymers with a hydrophilic and a responsive block can reversibly be assembled into micelles and vesicles and back to unimers [15,16]. The combination of two different stimuli-responsive blocks forms so called “schizophrenic” micelles, where depending on the conditions the micellar structure can be inverted [17–19]. Block copolymers are known to assemble in solution into spherical objects. At higher concentrations also fibrillar structures can be formed [20]. Especially worm-like, fibrillar structures are of interest for drug delivery [21,22], or as template for the preparation of nano-structured inorganic materials [23–25]. Since the core forming block has a great impact on the aggregate structure the use of stiff polymers as core is advantageous. Stiff polymers tend to form liquid crystalline structures. In assembled rod-coil block copolymers such phase can

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best be maintained in worm-like micelles. Hence, those structures are already formed at relatively low molecular weight of the stiff polymer [26]. As stiff block poly(*para*-phenylene), poly(fluorene), poly(*para*-phenylene vinylene) and poly(3-hexylthiophene) has been used [27,28]. Also special peptides have been reported to form helical, stiff structures [29].

In order to prepare rod-coil block copolymers mostly two different polymerization techniques have to be applied. The chemistry of the rod-like polymer block is determined by its structure [28]. The coil-like polymer block can subsequently be synthesized by Degenerative Transfer Radical Polymerization (DTRP) techniques [30–37]. Additionally, the block copolymers can be formed by linkage of preformed blocks [38,39]. The combination of stimuli-responsive polymers with rod-like polymers yielded systems that could be switched electrically between vesicles and micelles [40], could perform morphological changes [41] or could be used as combined temperature and pH sensor [42].

Stimuli-responsive fibrillar structures are essential in nature e.g. for blood clotting. Fibrinogen is activated by certain proteins to form Fibrin that assembles first into fibrils and then into a three dimensional network. Finally, this network is stabilized by additional cross-linking [43]. In order to prepare model systems that can assemble on temperature or pH stimulation rod-coil block copolymers with a responsive block were prepared. With respect to its more simple procedure and abstinence of a metal catalyst system nitroxide-mediated radical polymerization (NMRP) is a powerful tool to gain control over the polymerization of various monomers. In 2003 Hawker et al. reported the synthesis of rod-coil block copolymers by using an alkoxyamine functionalized biphenyl ester oligomer. This rod-like macro initiator was used for the NMRP of styrenes, acrylates and 1,3-dienes [44]. We reported about an alkoxyamine terminated poly(*para*-phenylene) (PPP) macroinitiator which was prepared using SPC and its application to form PPP-*b*-PS block copolymers. Thin films of these block copolymers showed a phase separation in nm-scale [45]. Recently the enhanced preparation of PPP macro initiators via SPC was described [46]. For the macro initiator synthesis a microwave system was applied. A decrease of the reaction time down to one minute could be achieved. Now, these macro initiators were applied in the polymerization of *N*-isopropyl acrylamide (NIPAAm) and 2-vinyl pyridine (2VP) to introduce a responsive segment.

2. Experimental section

2.1. Chemicals

Acetic anhydride was distilled and stored under argon. *N*-isopropyl acrylamide (NIPAAm, $\geq 98\%$, TCI) was purified by recrystallization from *n*-hexane. 2-Vinyl pyridine (2VP, $\geq 98\%$, Acros) was freshly distilled in vacuo before use. *N,N*-Dimethyl acetamide (DMAc, 99.5%, Acros), *N,N*-Dimethyl formamide (DMF, 99.5%, Grüssing) tetrahydrofuran (THF, 99.5%, Grüssing), xylene (99.5%, Grüssing) were used as received. All other reagents have been used as received.

2.2. Characterization

NMR spectra were recorded at 25 °C on a Bruker “Avance 500” spectrometer using CDCl₃ as solvent. SEC measurements of the PNIPAAm block copolymers were carried out using *N,N*-dimethyl acetamide (DMAc) containing 0.1% LiBr as eluent at a column temperature of 50 °C. The SEC set-up consists of a Merck Hitachi 655A-11 pump (flow rate: 1 mL/min), three PSS GRAM columns (particle size 10 μm, one guard: 8 × 50 mm, one with pore size 10² Å, 8 × 300 mm and one with pore sizes 10³ Å, 8 × 300 mm) from Polymer Standard Service (PSS), a Knauer “Smartline RI Detector 2300” refractive index detector and a Merck Hitachi L-4200 UV detector. Molecular weight and molecular weight distribution determinations of PPP macro initiators as well as P2VP block copolymers were carried out using SEC with THF as the solvent. A Merck Hitachi L-6200 pump (flow rate: 1 mL/min) and three columns (PSS-SDV guard: 5 μm, PSS-SDV 10⁵ Å, PSS-SDV 10³ Å) from Polymer Standard Service (PSS), a Knauer “Smartline RI Detector 2300” refractive index detector and a Merck Hitachi L-4200 UV detector were used. A calibration of the SEC set-ups was carried out using low dispersity poly(styrene) and poly(methyl methacrylate) standards. UV/Vis and turbidity measurements of aqueous block copolymer solutions (1 wt.%), in order to determine the critical temperature (T_c), were carried out using a PERKIN ELMER “Lambda 45” UV/Vis spectrophotometer. AFM images were recorded in tapping mode (AC Mode) with a “JPK Nanowizard® II” from JPK Instruments using a “NSC 15” Cantilever from Mikromash (resonance frequency: 320 kHz, force constant: 40 N m⁻¹). SEM images were recorded with a “Neon 40 ESB CrossBeam® FIB-SEM” from Zeiss.

2.3. Synthesis

Alkoxyamine functionalized poly[2,5-(2-ethylhexoxy)-1,4-phenylene-phenylene]s (EHPPP-TIPNO) macro initiators were prepared as recently described [46].

2.3.1. General procedure for the preparation of thermo-responsive coil-rod-coil block copolymers

A vacuum dried Schlenk tube was filled with argon and the macro initiator EHPPP-TIPNO (100 mg) as well as the monomer NIPAAm were added. After the addition of xylene the mixture was degassed by three freeze-pump-thaw cycles and the Schlenk tube was refilled with argon. The polymerization was started in a preheated oil bath at 135 °C for 48 h. Afterwards the reaction was stopped by cooling with liquid nitrogen and the polymer was dissolved in THF to transfer the solution into a

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