

Polymer Communication

Synthesis of PPP-*b*-PS block copolymers using a combination of Suzuki-polycondensation and nitroxide-mediated radical polymerization

Antje Britze ^a, Josemon Jacob ^b, Veena Choudhary ^b, Vera Moellmann ^a, Guido Grundmeier ^a, Heinrich Luftmann ^c, Dirk Kuckling ^{a,*}

^a Department Chemie, Universität Paderborn, D-33098 Paderborn, Germany

^b Centre for Polymer Science and Engineering, IIT Delhi, New Delhi-110016, India

^c Fachbereich Chemie und Pharmazie, Westfälische Wilhelms-Universität Münster, Corrensstr. 40, D-48149 Münster, Germany

ARTICLE INFO

Article history:

Received 10 May 2010

Received in revised form

8 September 2010

Accepted 9 September 2010

Available online 17 September 2010

Keywords:

Suzuki-polycondensation

Nitroxide-mediated radical polymerization

Block copolymers

π-Conjugated segments

ABSTRACT

The synthesis of π-conjugated Nitroxide-Mediated Radical Polymerization (NMRP)-macroinitiators by Suzuki-polycondensation in a one-step reaction has been investigated using conventional and microwave-heating in presence of a suitable terminating agent. Alkoxyamine-functionalized poly(*para*-phenylene)s were initially synthesized by Suzuki-polycondensation and then its block copolymer with styrene by NMRP. Molecular weight and molecular weight distribution of the polymers have been determined in SEC-measurements, while end-group determination was performed with MALDI-ToF-MS. Thin-layer-morphologies of the block copolymers were investigated using tapping-mode AFM.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer based electro-active materials gained increased interest because of their processability in spin-coaters and inkjet-printers. This allows for a low cost production of optoelectronic devices like field effect transistors (FETs) or light emitting diodes (LEDs) [1]. Conjugated polymers (CPs) are promising compounds in the fields of microelectronics, optoelectronics and photonics [2]. Although inherently insoluble, the solubility of CPs can be enhanced by introduction of flexible alkyl side chains [3], which helps to overcome π-π-interaction and precipitation [4]. A major challenge in the field of electronics is the minimization of current circuits for microelectronic devices. Conventional methods are based on photolithography, a so called "top-down" approach. The alternative "bottom-up" strategy cannot be realized without research on the controlled deposition of CPs. The mesoscopic ordering in π-conjugated systems influences the performance of optoelectronic devices like solar cells, LEDs and FETs.

The phase separation of block copolymers in the nm-scale is well known. Different morphologies in thin films have been investigated and characterized [5]. Therefore self-assembly of block copolymers

containing a π-conjugated segment is of great interest. The covalent bonding to a coil-like segment may simplify the processability of the material, while morphological effects on substrate surfaces may influence emission properties. The introduction of semi-conducting polymers like poly(*p*-phenylene), poly(thiophene) and poly(acetylene) into block copolymers can be accomplished using living ionic mechanisms. Poly(styrene)-*b*-poly(*p*-phenylene) and poly(methyl methacrylate)-*b*-poly(*p*-phenylene) were prepared this way [6–8]. As ionic polymerization techniques are quite demanding, our interest was focussed on the possibilities of controlled radical polymerizations. Especially nitroxide-mediated radical polymerization (NMRP) seems to be a useful tool because of its simple procedure in absence of any metal catalysts, ligands or sulphuric compounds. Boiteau et al. described the synthesis of a block copolymer of oligo(phenylene ethylene) and an oxadiazole-segment using TEMPO and proved the possibility to prepare electro-active materials using NMRP [9]. Further investigations were performed by Behl et al., leading to narrow distributed p-doped and n-doped block copolymers [10,11].

Herein we describe the synthesis of poly(*para*-phenylene)/poly(styrene) block copolymers, as well as the investigation of their macromolecular properties like molecular weight, molecular weight distribution, copolymer composition, end-group determination and thin-film morphology. PPP-*b*-PS films are interesting

* Corresponding author. Tel.: +49 5251 60 2171; fax: +49 5251 60 3245.

E-mail address: dirk.kuckling@uni-paderborn.de (D. Kuckling).

because of their honeycomb structure when deposited from CS_2 in humid atmosphere [12]. The Suzuki-polycondensation [13,14] has been used to produce end-group modified PPPs, which could be used as macroinitiators for anionic polymerization and synthesis of PPP-*b*-PEO and PPP-*b*-PS [15,16]. The aim of our work is the preparation of NMRP-macroinitiators from poly(*para*-phenylene) in as few steps as possible and in a low-demanding procedure. The successful combination of Suzuki-polycondensation and NMRP will be described.

2. Experimental part

2.1. Chemicals

The chemicals acetic acid (100%, VWR), ammonium hydroxide solution (28–30 wt%, Riedel-de Haen), bis(pinacolato)diboron (98%, Aldrich), bromine (Fluka), copper(II) acetate monohydrate (Fluka), 1,4-dioxane ($\text{H}_2\text{O} \leq 0.005\%$, Riedel-de Haen), 2-ethylhexyl bromide (95%, Aldrich), 1,4-dibromobenzene (98%, Aldrich), dimethylamine (40% solution in water, Fluka), hydroquinone (98%, Acros), isobutyraldehyde (Merck), manganese(III) acetate dihydrate (Merck), 2-methyl-2-nitropropane (99%, Acros), 1,1'-bis(diphenylphosphino)-ferrocen-dichloropalladium(0) ($\text{PdCl}_2(\text{dppf})$, Aldrich), tetrakis-triphenylphosphino-palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, 99%, Aldrich), phenylmagnesium chloride solution (1.8 M in THF, Fluka), sodium borohydride (Riedel-de Haen), THF ($\text{H}_2\text{O} \leq 0.005\%$, Fluka) and zinc powder (Aldrich) were used as received. 4-bromostyrene (96%, Acros) contains 0.1% 3,5-di-*tert*-butylcatechol as inhibitor, which has to be removed by elution above alumina (Al_2O_3 90, active neutral) prior to use.

2.2. Characterization

^1H -NMR-spectroscopy was performed to characterize low-molecular substances and to determine block copolymer composition using “AVANCE 500” spectrometer (Bruker). Elemental analysis data were obtained using “vario MICRO Cube” (elementar). Melting points were measured using a “BUCHI Melting Point B-545” apparatus at a heating rate of 1 $^{\circ}\text{C}/\text{min}$. Mass spectrometry in combination with gas chromatography was accomplished on an “AGILENT Technologies[®] 6890N gas chromatography system”, equipped with a mass selective “AGILENT Technologies[®] 5973 detector” and a DB 35ms column ($l = 30\text{ m}$, $d = 0.25\text{ mm}$, 0.25 μm film thickness of (35%-phenyl)-methyl polysiloxane) in an inert gas stream of 1.0 mL/min He. Determination of molecular weight and molecular weight distribution required SEC (Waters). The measurements were done in chloroform (containing 0.1 vol% triethylamine), using 3 styragel columns (10^4 – 10^6 \AA), BHT as internal standard and PS standards for calibration. MALDI-ToF mass spectrometry was performed on “reflex IV” (Bruker Daltonics[®]) in reflection mode (337 nm N_2 laser, acceleration voltage: 19 kV). The polymer samples were prepared in salt-free conditions from chloroform using DCTB matrix (matrix solution: 10 g/L, polymer solution 10 g/L, matrix:polymer 10:1 (v/v)). DSC was done using “Perkin Elmer Differential Scanning Calorimeter Pyris 1” in a temperature range from 50 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$ (heating rate: 20 $^{\circ}\text{C}/\text{min}$). AFM measurements were performed on “5100 Atomic Force Microscope” and “5500 Atomic Force Microscope” (Agilent Technologies) in tapping mode (cantilevers: NCS15/AIBS, spring constant: 46 N/m, resonance frequency: 325 kHz, MikroMasch). Thin film samples were prepared from polymer solutions in toluene (1 wt%) using dip-coating technique on silica wafers ($\{100\}$, 1 cm \times 2 cm).

2.3. Synthesis

2.3.1. *Synthesis of N-tert-butyl- α -isopropylnitron and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO) was accomplished as described in literature [17]*

2.3.1.1. *2,2,5-Trimethyl-3-(1'-(*p*-bromo)phenylethoxy)-4-phenyl-3-azahexane (*p*BrStTIPNO) (3).* The coupling of the styrene-derivative 4-bromostyrene with TIPNO in presence of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ and NaBH_4 was performed according to literature [2,18], yielding a highly viscous and colourless oil after column chromatography (silica gel, *n*-hexane/ethylacetate 100:1). Yield: 57%.

2.3.1.2. *2,5-dibromohydroquinone* [19]. In a 100 mL two-neck flask 5 g (45.4 mmol) hydroquinone were dissolved in 45 mL glacial acetic acid. 4.6 mL (90.8 mmol) bromine in 10 mL glacial acetic acid were added in drops at 0 $^{\circ}\text{C}$. After 4 h stirring at 35 $^{\circ}\text{C}$ the suspension was filtered. The solid was washed with cooled glacial acetic acid carefully. After reduction of the filtrate in *vacuo* further crystallization was achieved and the raw product was isolated as described before. Recrystallization from glacial acetic acid gave the pure substance. Yield: 65%.

2.3.1.3. *1,4-Bis-(2-ethylhexoxy)-2,5-dibromobenzene (1)*

In a 250 mL two-neck flask equipped with reflux condenser 3.954 g (14.7 mmol) 2,5-dibromohydroquinone were added to a solution of 8.288 g (60.0 mmol) potassium carbonate in 200 mL abs ethanol at room temperature under argon atmosphere. The mixture was heated to 60 $^{\circ}\text{C}$ and 7.0 mL (39.4 mmol) 2-ethylhexylbromide was added slowly. After stirring for 4 d at 80 $^{\circ}\text{C}$ 100 mL of saturated NaCl solution were added to the reaction mixture. The aqueous phase was extracted five times with 100 mL of *n*-hexane each. The combined organic layers were dried over magnesium sulphate and the solvent was removed in *vacuo*. To remove the excess of 2-ethylhexylbromide the raw product was dissolved in 5:1 mixture of ethanol/water and stirred over night at 80 $^{\circ}\text{C}$ in presence of 5 g (47.0 mmol) sodium carbonate and 10 mL (79.0 mmol) dimethylamine (40% solution in water). The mixture was extracted five times with 50 mL *n*-hexane each. The combined organic layers were dried over magnesium sulphate and the solvent was removed in *vacuo*. The product was purified by column chromatography (silica gel, 200 mL *n*-hexane, 500 mL *n*-hexane/ethylacetate 100:1) to give a colourless oil. Yield: 75%.

2.3.1.4. *4,4,5,5-Tetramethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)phenyl)-1,3,2-dioxaborolane (2)*

Under argon atmosphere 0.412 g (0.52 mmol) $\text{PdCl}_2(\text{dppf})$, 5.2 g (52.8 mmol) potassium acetate and 4.8 g (16.8 mmol) bis(pinacolato)diboron were weighed into a 100 mL two-neck flask. 2.0 g (8.4 mmol) 1,4-dibromobenzene and 40 mL dry 1,4-dioxane were added. After stirring at 100 $^{\circ}\text{C}$ for 24 h and a further night at room temperature the solvent was removed in *vacuo*. The residue was eluted using silica gel (*n*-hexane/ethyl acetate 50:1). After evaporation of the solvent in *vacuo*, traces of impurities were dissolved in small amounts of *n*-hexane and the product was removed by filtration. The pure product, a white solid, was dried in *vacuo*. Yield: 78%.

2.4. General procedure for Suzuki polycondensation

2.4.1. Variant A): Conventional

Under argon atmosphere 0.225 g (1.6 mmol) potassium carbonate, 0.200 g (0.4 mmol) **1**, 0.134 g (0.4 mmol) **2** and 0.016 g (0.04 mmol) **3** were weighed into a 25 mL two-neck flask equipped with a reflux condenser and wrapped with aluminium foil. After addition of 8 mL THF, 9 mg (0.008 mmol) $\text{Pd}(\text{PPh}_3)_4$, 2 mL bidist.

water and one drop Aliquat® 336, the mixture was stirred for 3 d at 70 °C. The polymer was isolated by precipitation in methanol and filtration. Purification involved repeated dissolution in chloroform, precipitation in methanol, filtration of the solid and drying in vacuo.

2.4.2. Variant B): Microwave synthesis

Microwave synthesis was performed in “open vessel” mode using a “CEM focused microwave™ synthesis system, type Discover”. Electrical power was set to a maximum of 100 W.

A 50 mL round bottom flask equipped with reflux condenser and argon balloon was charged with 0.700 g (5.0 mmol) potassium carbonate, 0.609 g (1.2 mmol) **1**, 0.414 g (1.2 mmol) **2**, 0.242 g (0.6 mmol) **3**, 0.026 g (0.002 mmol) $\text{Pd}(\text{PPh}_3)_4$, 5 mL THF and 20 mL bidist. water. The mixture was purged with argon shortly before one drop Aliquat® 336 was added. The reaction was accomplished using microwave heating at 70 °C while stirring for 1 h. The polymer was isolated by precipitation in methanol and filtration. Purification involved repeated dissolution in chloroform, precipitation in methanol, filtration of the solid and drying in vacuo.

2.5. General procedure for block copolymerization under NMRP-conditions

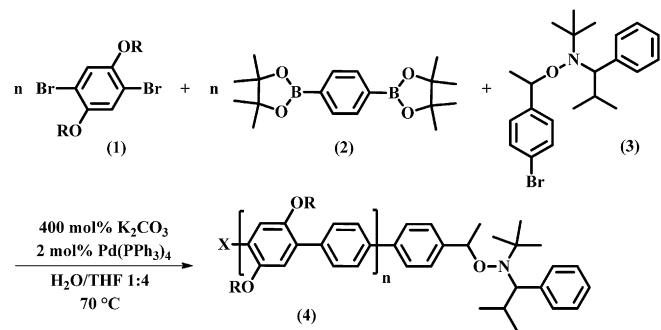
In a 25 mL Schlenck-flask a defined amount of PPP-macroinitiator was dissolved in styrene. The reaction mixture was degassed in three freeze–vacuum–thaw cycles. After refilling of the flask with argon and addition of a small amount of acetic anhydride the polymerization was started in a preheated oil-bath (120 °C). After 1–3 h the reaction mixtures were dissolved in chloroform and precipitated in a 10 fold excess of methanol. The polymers were isolated by filtration and purified by repeated solubilization in chloroform and precipitation in methanol. The products were dried in vacuo.

3. Results and discussion

The synthesis of block copolymers containing a π -conjugated poly(*p*-phenylene) segment can be accomplished using a combination of Suzuki-polycondensation (SPC) and nitroxide-mediated radical polymerization (NMRP). Suzuki-coupling realizes the arylation of organo boron compounds with aryl bromides. This technique allows *para*-coupling of aromatic units if bifunctionalized monomers are used. The aimed introduction of end-groups efforts the presence of a monofunctional termination agent in the reaction mixture. If this end-group should provide further chain growth the termination agent has to be a difunctional compound. In the documented case a bromine-function allows the end-capping of the macroinitiator, while an alkoxyamine group will initiate a controlled radical polymerization. The amount of the termination agent in the reaction mixture limits the molecular weight of the final polymers.

3.1. Synthesis of starting materials

The introduction of a TIPNO-functionality into a growing poly(*p*-phenylene) chain during SPC requires a termination agent with alkoxyamine structure and a bromide in *p*-position of the initiating styrene-derivative. The synthesis of *p*BrStTIPNO **3** was accomplished in presence of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ and NaBH_4 . After intensive column chromatography the colourless oil was isolated in a yield of 57%. To overcome the problem of π – π -stacking and low solubility of the poly(*p*-phenylene) segment at least one of the monomers should provide an alkyl side chain. Herein the dibromo-functionalized monomer was the carrier of the solubility enhancing groups. The synthesis of 1,4-bis(2-ethylhexoxy)-2,5-dibromobenzene **1** can be achieved by starting



Scheme 1. Synthesis of EHPPP-TIPNO (4) using SPC.

from the bromination of hydroquinone and subsequent Williamson-etherification between 2,5-dibromohydroquinone and 2-ethylhexyl bromide. Useful organo boron compounds for SPC are boronic acids and their esters. Latter was used herein because of the tendency of boronic acids for self-condensation [20]. Pinacolester was chosen instead because of its ease of purification using column chromatography. Similar to Miyaura et al., who performed the first one-step-synthesis of aryl boronic esters using aryl halides [21], a transfer metal-catalyzed cross-coupling between commercially available bis(pinacolato)-diboron and 1,4-dibromobenzene towards **2** was accomplished. A white solid was isolated in yields of 78% and could be stored at –22 °C for several weeks.

3.2. Synthesis of TIPNO-functionalized EHPPP-macroinitiators

The monomers **1** and **2** in 1:1 ratio were coupled in presence of the termination agent **3** towards TIPNO-terminated poly[2,5-(2-ethylhexoxy)-1,4-phenylene-phenylene]s (EHPPP-TIPNO) (**4**) (Scheme 1). The resulting polymer was labelled according to the nomenclature of poly(*p*-phenylene vinylene)s [22].

The concentration of *p*BrStTIPNO (**3**) was varied between 10 mol % and 30 mol %. The maximum reaction temperature was set to 70 °C to avoid thermal decomposition of the alkoxyamine. The preparations were performed in presence of $\text{Pd}(\text{PPh}_3)_4$. The solvent mixture contained dist. water and THF in ratio 1:4. The polymers were isolated by repeated precipitation in methanol and dried in vacuo. The products showed a greyish colour in substance, their chloroform solutions gave a violet shade. The reactions were performed in oil-bath (conventional SPC) or using microwave-heating (“open vessel” mode). In the first case long reaction times up to 3 d were necessary to obtain oligomers with a degree of polymerization (DP) of 6 (12 aromatic units). The influence of the amount of termination agent is given in Table 1, entries 1–3. An increase of termination agent (**3**) resulted in decreasing molecular weight and molecular weight distribution. Typical SEC traces are shown in Fig. 1.

Table 1
synthesis of EHPPP-TIPNO (4), $T = 70$ °C, solvent: $\text{H}_2\text{O}/\text{THF}$ 4:1.

entry	sample	heating source	time [h]	macroinitiator EHPPP-TIPNO			
				[<i>p</i> BrStTIPNO] [mol%]	M_n^* [g/mol]	M_w/M_n^*	DP
1	4a	oil-bath	72	10	3400	2.01	8
2	4b	oil-bath	72	20	3100	1.86	7
3	4c	oil-bath	72	30	2500	1.73	6
4	4d	MW-oven	1	30	3300	1.68	8
5	4e	MW-oven	1	30	2400	1.42	6
6	4f	MW-oven	1	30	2400	1.56	6

*SEC: CHCl_3/PS -standards, RI-detection.

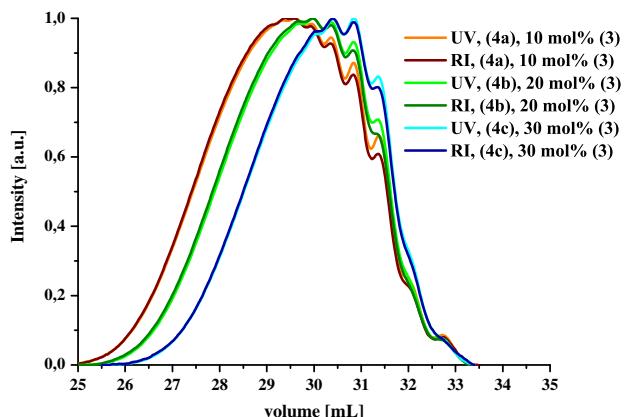


Fig. 1. Synthesis of macroinitiators (**4a**), (**4b**) und (**4c**) subjected to $[p\text{BrStTIPNO}]$ (**3**) in mol%, SEC: CHCl_3/PS -Standards, RI/UV-detection (325 nm).

The amount of short chains should be decreased when the reaction reaches full conversion. This goal could not be achieved due to increased viscosity of the reaction medium, which constrains the diffusion of the reaction partners towards each other. Another problem is the solubility of the polymer in chloroform, which can be improved by the introduction of alkyl side chain but still remains low in comparison with really good soluble polymers like polystyrene. Precipitation disturbs the polycondensation

equilibrium. Finally the lifetime of the catalyst is restricted to only a few catalytic cycles.

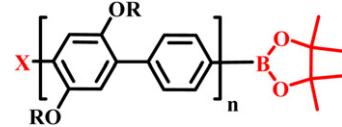
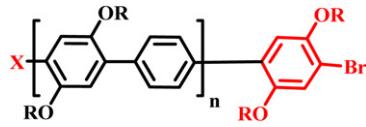
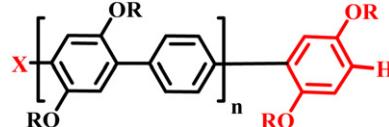
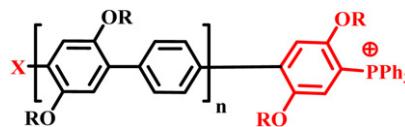
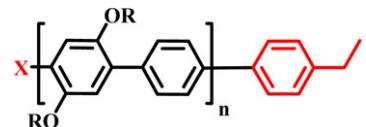
Microwave synthesis becomes more and more important in modern organic synthesis. Commercially available instruments operate at a radiation frequency of 2.45 GHz, which is in accordance with a wavelength of 12.24 cm. The energy of the irradiation is much too low to induce a breakage of chemical bonds. The electric part of the electromagnetic radiation forces dipoles and ions to align in an oscillating field. This results in an energy transfer in terms of heat [23]. Therefore microwaves allow efficient internal heating of reaction mixtures. The acceleration of reaction rates can be explained using the Arrhenius-Equation. Microwave synthesis is a very useful tool for the performance of Suzuki-couplings, because of the increased lifetime of the Pd-catalyst. The walls of the reaction vessel remain quite cold in single-mode microwave ovens, leading towards a decrease in catalyst-destructive side reactions [23]. Since a short time polymer chemists are performing Suzuki-polycondensation reactions successfully in microwave oven [24,25]. Within this work a single-mode microwave system was used to prepare EHPPPs. Results are given in Table 1, entries 4–6. Microwave-heating results in a great reduction of the reaction time from 72 h to 1 h, while the molecular weight of the polymers remains almost constant. Accordingly a decrease in molecular weight distribution can be observed. One disadvantage of the synthesis in the microwave oven may be a small loss in yield. All microwave-reactions were performed in presence of 30 mol% of termination agent **3** to ensure effective end-capping of the polymers. The

Table 2a
possible end-groups X in EHPPP (**4**).

end-group X	structure
functionality	short cut
pinacolester	E-B
bromide	Br
hydrogen after H/Br-exchange	H
cationization due to Br/PPh3-exchange	PPh_3^+
TIPNO-functionalization; ethylbenzene after fragmentation	PhTIPNO

Table 2b

Possible end-groups Y in EHPPP (4).

end-group Y	functionality	short cut	structure
pinacolester		B	
brominated monomer		E-Br	
hydrogen after H/Br-exchange		E-H	
cationization due to Br/PPh3-exchange		E-PPh3+	
TIPNO-functionalization; ethylbenzene after fragmentation		TIPNO	

determination of the end-groups was accomplished using MALDI-ToF mass spectrometry. In presence of the electron donating matrix DCTB [26] PPPs can be ionized easily without any use of additional salt. One problem is the strong absorption of these polymers at a wavelength of 337 nm, corresponding to the N₂-laser which is responsible for matrix desorption. The absorption of energy leads to the generation of radicals by photoionization and fragmentation of the sample [27]. Therefore difficulties in interpretation of the spectra may arise. Other problems are group-transfer reactions observed during Suzuki-coupling, which results in end-group modifications. The exchange of bromide against hydrogen was observed already as well as the cationization of chains due to Br/PPh₃ exchange [27]. The aim of our work was the termination of EHPPP (4) with alkoxyamine-groups. Those functionalities are well known to fragment during treatment with laser light [28]. In this case ethylbenzene-residues should be observed at the chain ends. Tables 2 a and 2b summarize the possible end-groups of EHPPPs (4) after aforementioned synthesis. Various combinations of possible end groups, which can be assigned to the MS spectra, are given in Table 3. Calculations of their molecular weight are explained in the supporting information.

Fig. 2 shows the mass spectra for EHPPP samples synthesized conventionally and using microwave, respectively. The synthesis using oil-bath within 3 d leads to much more end-group modifications as can be seen from the complex spectrum (Fig. 2 a). Additionally to the lower polydispersity values this observation indicates the advantages of SPC using microwave synthesis once again.

In both MS spectra the main signals can be assigned to mono-TIPNO-terminated PPP-chains (distribution "3" in Fig. 2). Taking the easy cleavage of the nitroxide into account the term "TIPNO-terminated" is used for polymer chains which show an ethylbenzene-residue in the MALDI-ToF-MS spectra. One of the side-distributions could belong to those mono-functionalized macroinitiators, too. But termination with bromide and triphenylphosphine-groups would fit the calculation just as well. The side-distributions "2" and "4" correspond to "dead" chains (Table 3). Bromide-, hydrogen- or PPh₃-terminated polymers are not suitable for further block copolymerizations at NMRP-conditions. A fifth, low intensive, group of signals could not be assigned exactly and was observed in microwave synthesized samples. The results of MALDI-ToF mass spectrometry

Table 3

End-group determination of EHPPP (4) using MALDI-ToF-MS.

entry	M(EG ₁ +EG ₂) [g/mol]	possible combinations of end-groups	
		X = EG ₁	Y = EG ₂
1	370	PPh ₃ ⁺	TIPNO
		PhTIPNO	E-PPh ₃ ⁺
2	269	Br	E-PPh ₃ ⁺
		PPh ₃ ⁺	E-Br
3	187	Br	TIPNO
		PhTIPNO	E-Br
		H	E-PPh ₃ ⁺
		PPh ₃ ⁺	E-H
4	86	Br	E-Br
5	63	—	—

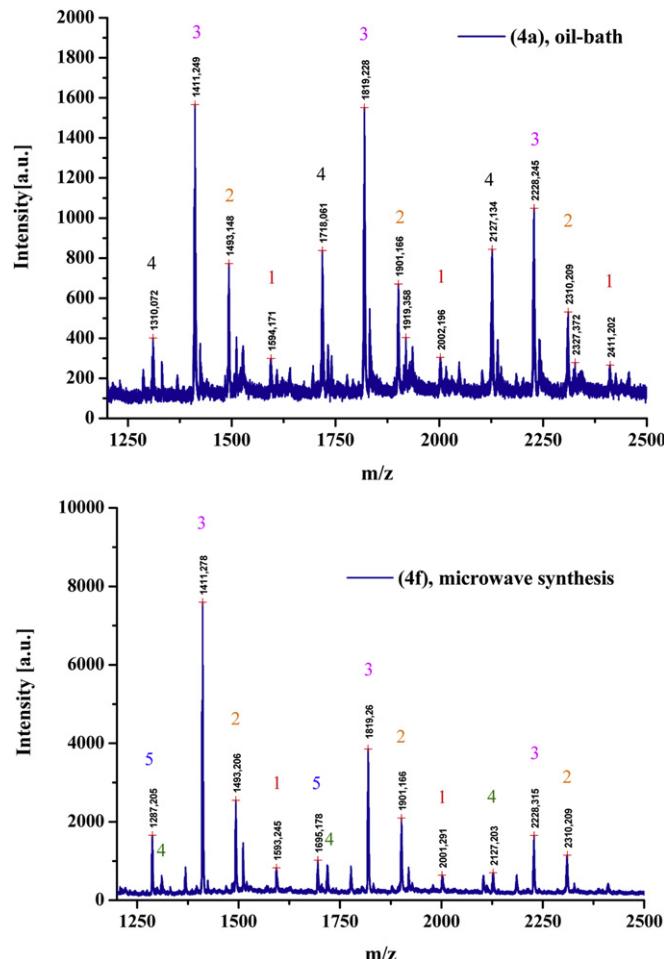


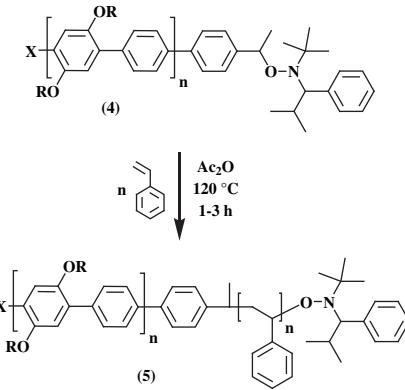
Fig. 2. MALDI-ToF mass spectra of EHPPP, (7a): 10 mol% *p*BrStTIPNO (3), $M_{n,GPC} = 3400$ g/mol, $M_w/M_n = 2.01$, (7b): 30 mol% *p*BrStTIPNO (3), $M_{n,GPC} = 2400$ g/mol, $M_w/M_n = 1.56$.

indicate a partial mono-functionalization of growing EHPPP chains with an alkoxyamine group during SPC between compounds (1) and (2) in presence of (3). Those polymers can be used as macroinitiators in further polymerizations at NMRP conditions to prepare diblock copolymers.

3.3. Synthesis of EHPPP-block copolymers using NMRP

The synthesis of rod-coil block copolymers (5) from EHPPP-macroinitiators (4) is shown in Scheme 2. Details of the synthesis are summarized in Table 4. After precipitation of the block copolymers and drying in *vacuo* the molecular weights of the samples were determined in SEC measurements.

To be sure that block copolymerization was really successful it was necessary to combine RI and UV detection. The absorption of the PS segment can be observed at a wavelength of 260 nm, while two other absorption maxima (290 nm, ~345 nm) belong to the EHPPP block. Variations in the block length of the π -conjugated segment result in a shift of the absorption maximum at about 345 nm. Hence, the UV-vis-detection during the SEC-measurements was performed at a wavelength of 325 nm to prove the successful block copolymerization. Fig. 3 shows the SEC traces of the EHPPP/PS-block copolymers (5g,h,i) and (5d,e,f) prepared from the macroinitiators (4e) and (4c), respectively.



Scheme 2. Synthesis of EHPPP-*b*-PS (5) under NMRP-conditions.

The groups of polymers shown in Fig. 3 A and B differ in the reaction time of NMRP. RI-detection gave a bimodal signal always, even if the intensity of the signal at higher elution volume can be quite low. It corresponds to unreacted EHPPP-chains remaining in the sample. The peaks at lower elution volume are characterized by a narrow peak width. This indicates controlled chain growth. In combination with UV detection it becomes clear, that the high molecular weight shares of the samples absorb light at 325 nm. The EHPPP macroinitiators formed a block copolymer with PS under NMRP conditions. The molecular weight of the block copolymers increased with increasing reaction time during NMRP. The comparison of the RI-signal intensity of unreacted macroinitiator in Fig. 3 A and B) shows a higher amount of unreactive chains in the second case. Macroinitiator (4c) was synthesized using oil-bath heating for 3 d, while macroinitiator (4e) was prepared within 1 h in a microwave oven. It is obvious that microwave synthesis is the more efficient method to prepare TIPNO-terminated PPP-macroinitiators in a one-step reaction. The results of the molecular weight determinations are summarized in Table 5. Decreasing polydispersities after the NMRP reaction in comparison to the macroinitiators indicates the controlled chain growth of the second block. In general, the polymerization yields of the NMRP are higher, if PPP-macroinitiators prepared via microwave synthesis are used. This indicates the better efficiency of end-capping with the alkoxyamine-group using this technique. The amount of chain-ends which are capable of further propagation is lower in the time-consuming conventional synthesized TIPNO-terminated PPPs. As the degree of the polymerization is defined as the ratio of monomer to initiator, the chain length of the PS segment will increase faster if these conventional prepared macroinitiators are used in the

Table 4
synthesis of EHPPP-*b*-PS (5) – reaction parameters, $T = 120$ °C, in bulk.

Sample	EHPPP-macroinitiator	styrene			t [h]	yield			
		#	m_{ini} [g]	n_{ini} [mmol]	V_{mon} [mL]	m_{mon} [g]	n_{mon} [mmol]	m_{pol} [g]	%
5a	4b	0.045	0.01	1.0	0.906	8.7	1	0.122	8
5b		0.043	0.01	1.0	0.906	8.7	2	0.186	15
5c		0.033	0.01	1.0	0.906	8.7	3	0.188	17
5d	4c	0.039	0.01	1.0	0.906	8.7	1	0.081	5
5e		0.040	0.01	1.0	0.906	8.7	2	0.135	10
5f		0.051	0.01	1.0	0.906	8.7	3	0.227	19
5g	4e	0.101	0.04	2.0	1.812	17.4	1	0.364	14
5h		0.108	0.04	2.0	1.812	17.4	2	0.801	38
5i		0.092	0.04	2.0	1.812	17.4	3	0.688	33
5j	4f	~0.1	~0.04	0.5	0.453	4.3	1	0.132	29
5k		~0.1	~0.04	0.5	0.453	4.3	2	0.081	17
5l		~0.1	~0.04	0.5	0.453	4.3	3	0.292	64

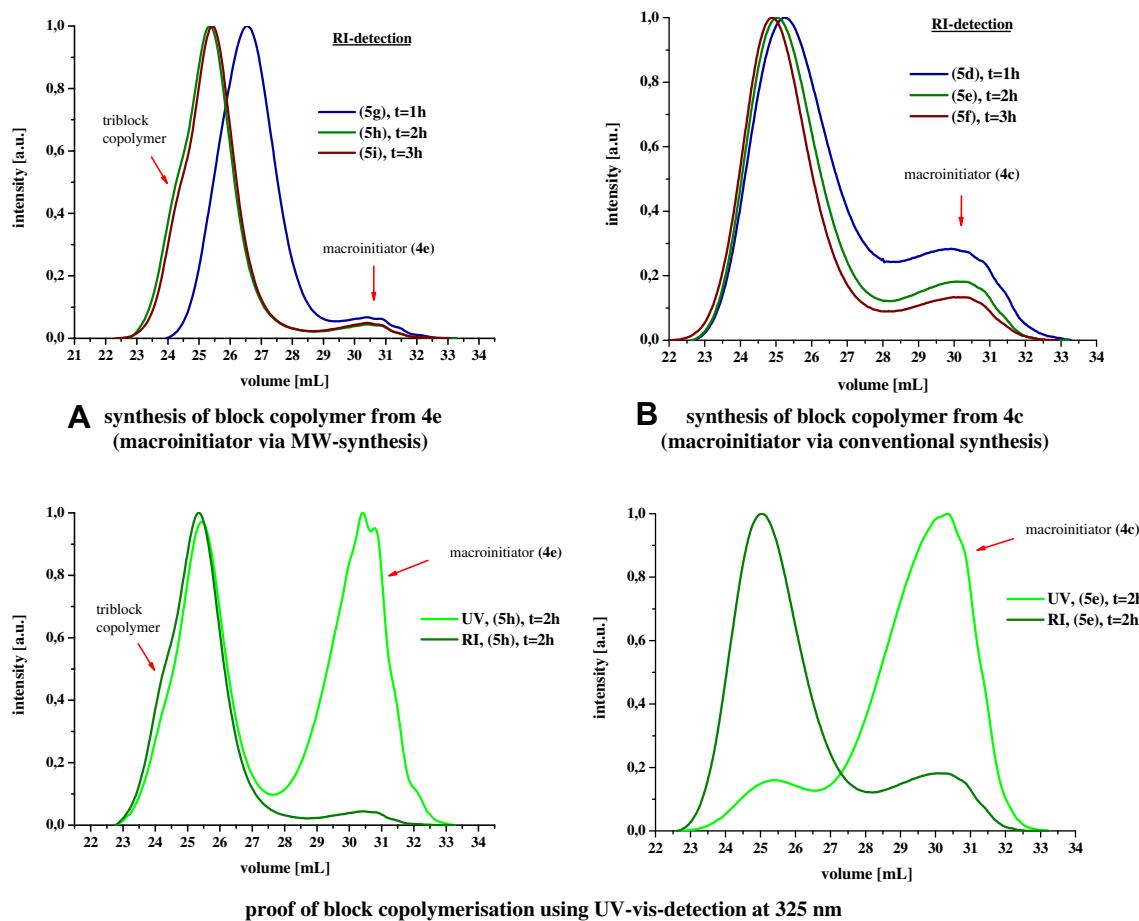


Fig. 3. SEC traces of EHPPP-*b*-PS ((5g–i), (5d–f)) from EHPPP-macroinitiators ((4e), (4c)), SEC: CHCl_3/PS -standards, RI/UV-detection (325 nm).

following block copolymer synthesis. This leads to a quick increase of the viscosity of the reaction media and therefore limits the conversion of styrene. The ratio of block length of EHPPP and PS were determined using $^1\text{H-NMR}$ spectroscopy. If this ratio was calculated from the SEC-measurements strongly varying results had been obtained.

These differences may result from the calibration with PS-standards in the SEC experiment. The hydrodynamic volume of EHPPP and PS differs, so it can be assumed that the molecular weight of the stiff π -conjugated chains will be underestimated. Another and much more important problem is the possible

aggregation of block copolymers which feign too high molecular weights for the products and distort the calculation of the DP of the PS segment. Therefore the EHPPP/PS-ratios calculated from $^1\text{H-NMR}$ spectra should mimic the real ratios best. DSC measurements indicate the glass transition temperature of the block copolymers round about 90 °C (Fig. 4). Glass transition of pure PS can be observed at 100 °C [29]. No melting temperature was observed between 50 and 250 °C. The thermal behaviour of the block copolymers is dominated by the PS segment. For comparison Fig. 4 shows a typical DSC curve of a pure EHPPP macroinitiator, indicating melting at 217 °C and recrystallization during cooling

Table 5
composition of block copolymers/EHPPP-*b*-PS (5), * SEC: CHCl_3/PS -standards, RI-detection n = multiple of PS-block length after calculation from SEC results in comparison with $^1\text{H-NMR}$ -data.

sample	EHPPP-macroinitiator				EHPPP- <i>b</i> -PS/block copolymer				
	#	M_n^* [g/mol]	M_w/M_n^*	DP	M_n^* [g/mol]	M_w/M_n^*	$^1\text{H NMR}$ EHPPP:PS	SEC* EHPPP:PS	n
5a	4b	3100	1.86	7	36 800	1.27	1:5	1:46	9.2
5b					55 200	1.26	1:10	1:70	7.0
5c					74 300	1.31	1:7	1:97	13.8
5d	4c	2500	1.72	6	33 800	1.35	1:6	1:50	8.3
5e					39 300	1.30	1:9	1:57	6.3
5f					42 600	1.31	1:12	1:64	5.3
5g	4e	2400	1.41	6	20 800	1.23	1:11	1:29	2.6
5h					41 500	1.24	1:25	1:62	2.5
5i					39 800	1.22	1:24	1:60	2.5
5j	4f	2400	1.56	6	7200	1.28	1:2	1:7	3.5
5k					3200	1.50	1:0.666	1:1	1.5
5l					17 400	1.21	1:7	1:24	3.4

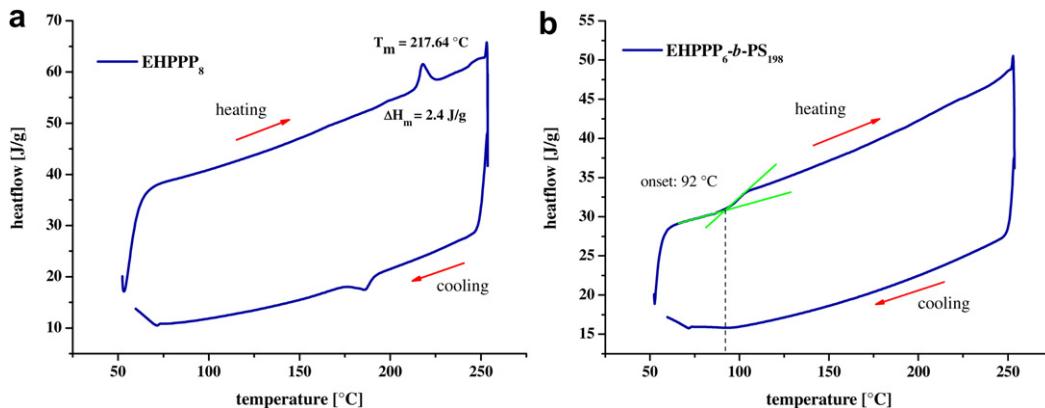


Fig. 4. DSC- a) macroinitiator: $M_n = 3500$ g/mol, $M_w/M_n = 2.01$; b) block copolymer: $M_n = 43\,100$ g/mol, $M_w/M_n = 1.19$, SEC: CHCl_3/PS -standards, RI-detection.

between 190 °C and 175 °C, too. The dominating coil-like segments in the block copolymer disturb the parallel orientation of the rigid segments towards each other. Therefore no melting or tendency of crystallization, respectively, can be observed in the final material (Fig. 4 b).

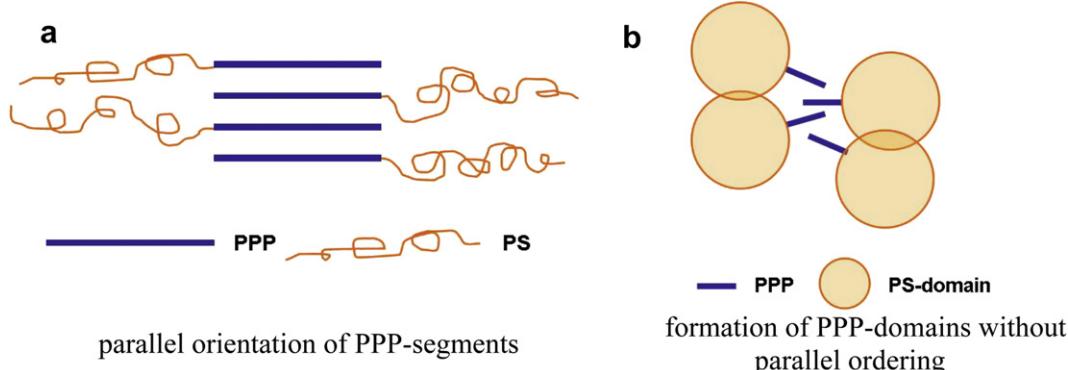
The surface morphology of EHPPP/PS-block copolymers were investigated using tapping mode AFM. Thin film samples were prepared on silica substrates by dip-coating of 1 wt% polymer solutions in toluene and following free solvent evaporation. Scheme 3 a sketches the optimal orientation of EHPPP-*b*-PS chains towards each other, leading to a dense package of EHPPP segments [6]. It gives rise to phase separation in nm-scale. The DSC-measurements already indicated that the ratio of the block length is not optimal to allow this ideal orientation. In our case we should rather expect a formation of dominating PS-domains like it is shown in Scheme 3 b.

Fig. 5 shows the AFM images of three block copolymer samples with different EHPPP content. EHPPP-*b*-PS (**5e**) contains an EHPPP segment of 12 aromatic units and a PS block with a DP of 54. The EHPPP amount corresponds to 10 mol%. Strongly disordered and very short nm-sized rods can be observed. As expected a high amount of PS disturbs proper phase separation. If the amount of EHPPP is increased to 33 mol%, as shown in (Fig. 5 B) on block copolymer (**5j**), parallel ordering of short rods in small domains arises. The distance between side-by-side lying rods was 21 nm. A surprising result showed the AFM images of block copolymer (**5f**) (Fig. 5 C). At EHPPP amount of 3 mol% no phase separation was expected. Nevertheless well aligned continuous pre-lamellar structures and spherical aggregates were observed. The width of the fibrils is 33 nm in average. Their length differs between 230 nm

and 340 nm. The “knots” measure 105 nm in width and 135 in length.

4. Summary

The synthesis of π -conjugated NMRP-macroinitiators was accomplished in a one-step reaction. The advantageous use of microwave synthesis could be shown in SPC between 4,4,5,5-tetramethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)phenyl)-1,3,2-dioxaborolane and 1,4-bis-(2-ethylhexoxy)-2,5-dibromobenzene in presence of the termination agent 2,2,5-trimethyl-3-(1-(*p*-bromo)phenylethoxy)-4-phenyl-3-azahexane (*p*BrStTIPNO). Polydispersities of 1.42 were realized, which is not natural for polycondensation reactions. The molecular weight of the obtained poly[2,5-(2-ethylhexoxy)-1,4-phenylene-phenylene]s (EHPPPs) was varied by the amount of a mono-brominated alkoxyamine. Macroinitiators with a molecular weight of 2000 g/mol to 5600 g/mol have been isolated, corresponding to 10–26 coupled phenylene rings. Mono-functionalization of EHPPP with the alkoxyamine was proved using MALDI-ToF-MS. Those macroinitiators have been used to prepare block copolymers in subsequent nitroxide-mediated radical polymerization (NMRP) with styrene. SEC in combination of RI- and UV-detection revealed the successful synthesis of the block copolymers EHPPP-*b*-PS. The amount of EHPPP in the block copolymers varied between 2 mol% and 50 mol% according to ^1H -NMR spectroscopy. AFM images of the resulting block copolymers in thin films on silicon wafers show phase separation in nm-scale. Short and disordered rods were observed as well as preliminary stages of continuous and parallel ordered fibrils and spherical aggregates.



Scheme 3. Orientation of rod-coil block copolymer chains towards each other in solid phase.

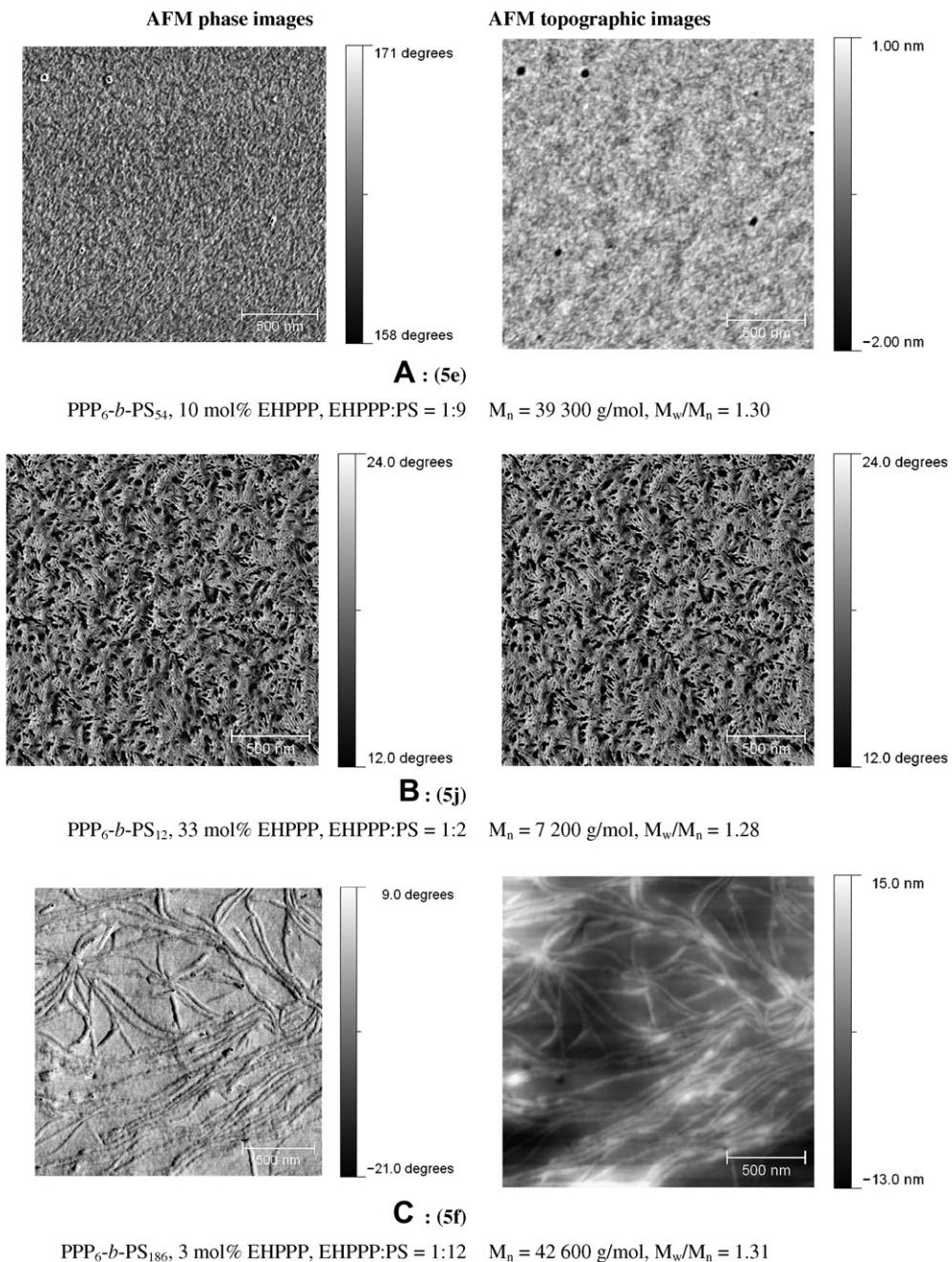


Fig. 5. Tapping mode-AFM pictures of EHPPP-*b*-PS (5), samples prepared from polymer solutions in toluene (1 wt%) using dip-coating technique on silica wafers ($\{100\}$, 1 cm \times 2 cm).

Acknowledgement

We thank Dr. Ingmar Bauer (TU Dresden) for GC-MS. "Fonds der Chemischen Industrie", DFG (SFB 287) "Reactive Polymers" and DAAD are gratefully acknowledged for financial support.

References

- [1] Deng L, Furuta PT, Garon S, Li J, Kavulak D, Thompson ME, et al. *Chem Mater* 2006;18:386–95.
- [2] Hadzioannou G, van Hutten PF, editors. *Semiconducting polymers: chemistry, physics and engineering*. Weinheim: Wiley-VCH; 2000.
- [3] Wang C, Kilitziraki M, MacBride JAH, Bryce MR, Horsburgh LE, Sheridan AK, et al. *Adv Mater* 2000;12:217–22.
- [4] Kutzner F. *Synthese und Charakterisierung von Monomeren und deren Suzuki-Polykondensation*, Dissertation. Berlin: Freie Universität; 2003.
- [5] Förster S, Plantenberg T. *Angew Chem* 2002;114:712–39.
- [6] Leclère P, Parente V, Brédas JL, François B, Lazzaroni R. *Chem Mater* 1998;10:4010–4.
- [7] Zhong XF, François B. *Makromol Chem Rapid Commun* 1988;9:411–6.
- [8] Lazzaroni R, Leclère P, Couturiaux A, Parente V, François B, Brédas JL. *Synth Met* 1999;102:1279–82.
- [9] Boiteau L, Moroni M, Hilberer A, Werts M, de Boer B, Hadzioannou G. *Macromolecules* 2002;35:1543–8.
- [10] Behl M, Hattemer E, Brehmer M, Zentel R. *Macromol Chem Phys* 2002;203:503–10.
- [11] Behl M, Zentel R. *Macromol Chem Phys* 2004;205:1633–43.
- [12] Widawski G, Rawiso M, François B. *Nature* 1994;369:387–9.
- [13] Rehahn M, Schlüter AD, Wegner G, Feast WJ. *Polymer* 1989;30:1054–9.
- [14] Schlüter AD. *J Polym Sci Polym Chem* 2001;39:1533–56.
- [15] Francke V, Räder HJ, Geerts Y, Müllen K. *Macromol Rapid Commun* 1998;19:275–81.

- [16] Marsitzky D, Brand T, Geerts Y, Klapper M, Müllen K. *Macromol Rapid Commun* 1998;19:385–9.
- [17] Benoit D, Chaplinski V, Braslau R, Hawker CJ. *J Am Chem Soc* 1999;121:3904–20.
- [18] Krause T, Habicher WD, Messerschmidt M, Voit Bl. *Design Monom Polym* 2003;4:391–7.
- [19] Tietze LF, Eichler T. *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, 2. Auflage. Stuttgart: Georg Thieme Verlag; 1991.
- [20] Sakamoto J, Rehahn M, Wegner G, Schlüter AD. *Macromol Rapid Commun* 2009;30:653–87.
- [21] Ishiyama T, Murata M, Miyaura N. *J Org Chem* 1995;60:7508–10.
- [22] Babel A, Jenekhe SA. *Macromolecules* 2004;37:9835–40.
- [23] Kappe CO. *Angew Chem Int Ed* 2004;43:6250–84.
- [24] Galbrecht F, Bünnagel TW, Scherf U, Farrell T. *Macromol Rapid Commun* 2007;28:387–94.
- [25] Tsami A, Yang XH, Farrell T, Neher D, Holder E. *J Polym Sci Polym Chem* 2008;46:7794–808.
- [26] Ulmer L, Torres Garcia G, Mattay J, Luftmann H. *Eur Mass Spectrom* 2000;6:57–60.
- [27] Remmers M, Müller B, Martin K, Räder HJ, Köhler W. *Macromolecules* 1999;32:1073–9.
- [28] Bothe M. *Synthese von Nitroxiden und Alkoxyaminen und deren Einsatz in der kontrollierten radikalischen Polymerisation*, Dissertation. Clausthal: Technische Universität; 2003.
- [29] Brandrup J, Immergert EH. *Polymer handbook*. 3rd ed., vol. 13. JohnWiley& Sons; 1989.