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Synthesis of Partially Protected Block Copolymers Based on 4-Hydroxystyrene Using NMRP and a Sequence of Polymer Analogous Reactions

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ABSTRACT: We present the synthesis and characterization of a family of partially protected block copolymers and their precursors synthesized by means of nitroxide mediated radical polymerization (NMRP) and a sequence of quantitative and orthogonal polymer analogous reactions. The target materials consist of an unprotected 4-hydroxystyrene block and a *tert*-butoxycarbonyl (BOC) or a *tert*-butyl (TBU) protected block. Corresponding precursor block copolymers exhibit low polydispersity indexes (PDI) (<1.36) and show well-defined compositions of their blocks. Techniques like NMR, FT-IR, GPC, DSC, and TGA were applied in order to verify structure, compositions, molar masses, molecular weight distributions, and thermal properties. These materials are promising candidates for self-assembly in thin films and subsequent photolithographic patterning applications.

Introduction

There is an increasing interest in the formation of smaller and smaller features beyond the limits imposed by photolithography.[1] To this end, new promising approaches combine bottom-up (self-assembly of block copolymers)[2] with top-down patterning techniques, intending the creation of features with smaller sizes and additionally the preparation of regular domains on a surface.[3]

Block copolymers have emerged as a challenging alternative for miniaturization[4] as they can self-assemble into highly regular structures of mesoscopic dimensions. By changing composition, molar masses, molecular architecture, and chemical structures, the size and type of ordering can be varied.[5] Moreover, specific functionalities can additionally be incorporated into the polymer structure, imparting the polymer special properties for greater versatility and further application perspectives (e.g., laboratory on a chip, storage device etc.).[4]

In this context many contributions have already been made by different research groups demonstrating the applicability of block copolymers for nanotechnology and miniaturization.[6]

Defined alignment and regular structures were achieved by controlling both the orientation and the long-range order of the block copolymers.[6] Steps in this direction could be accomplished using the influence of external electric fields,[7–9] shear forces,[10,11] crystallization,[12,13] and patterned surfaces[14,15] or by solvent evaporation at a controlled rate.[16–18] A prominent example is the block copolymer system poly(styrene-*b*-methyl methacrylate), which could be oriented perpendicularly to the substrate by different techniques, e.g., using electrical fields, and controlled interfacial interactions.[7,8] Additionally, the long-range order over several micrometers lateral distance could be performed by using a photolithographically prestructured substrate.[19] So far, the top-down and bottom-up approaches have been combined applying block copolymers with a very narrow molar mass distribution mainly prepared by anionic polymerization.[20] One of the drawbacks of this technique is the required preparative effort and, furthermore, the limited scope of functionalities possibly integrated in the macromolecules. An alternative to anionic polymerization is the use of controlled radical polymerization techniques like atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMRP),[21] or reversible addition–fragmentation transfer polymerization (RAFT), which are much more tolerant toward functional monomers. Furthermore, they require much less strict reaction conditions than anionic polymerization and are therefore much more easily to perform.

Polymers like poly(4-*tert*-butoxycarbonyloxystyrene) and poly(4-*tert*-butyloxystyrene) are well established photoresists and have been applied in different manufacturing processes like, e.g., the fabrication of microchips and electronic devices.[22]

Here, we present a family of partly protected block copolymers which have the ability for self-assembly in thin films and the potential for photolithographic patterning modifications. The synthesized materials consist of a poly(4-hydroxystyrene) block and a BOC- or TBU-protected poly(4-hydroxystyrene) block (Figure 1). They are characterized by a varying ratio of the molar masses of their blocks and are therefore capable to form different microstructures.[23]

These features make the synthesized block copolymers promising for applications in nanoscience and nanotechnology. Their synthesis and characterization are here emphasized.

Experimental Section

1. Materials. 4-Acetoxystyrene (97%, Aldrich) and 4-*tert*-butoxystyrene were distilled under reduced pressure prior to use. Diethylene glycol dimethyl ether (diglyme) (99%, Aldrich) was stirred over calcium hydride for 12 h and distilled under reduced pressure.

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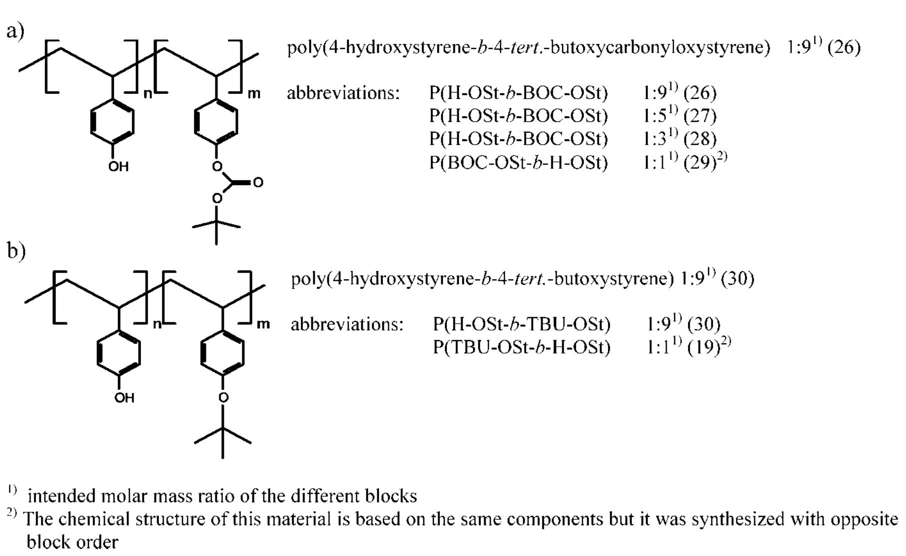
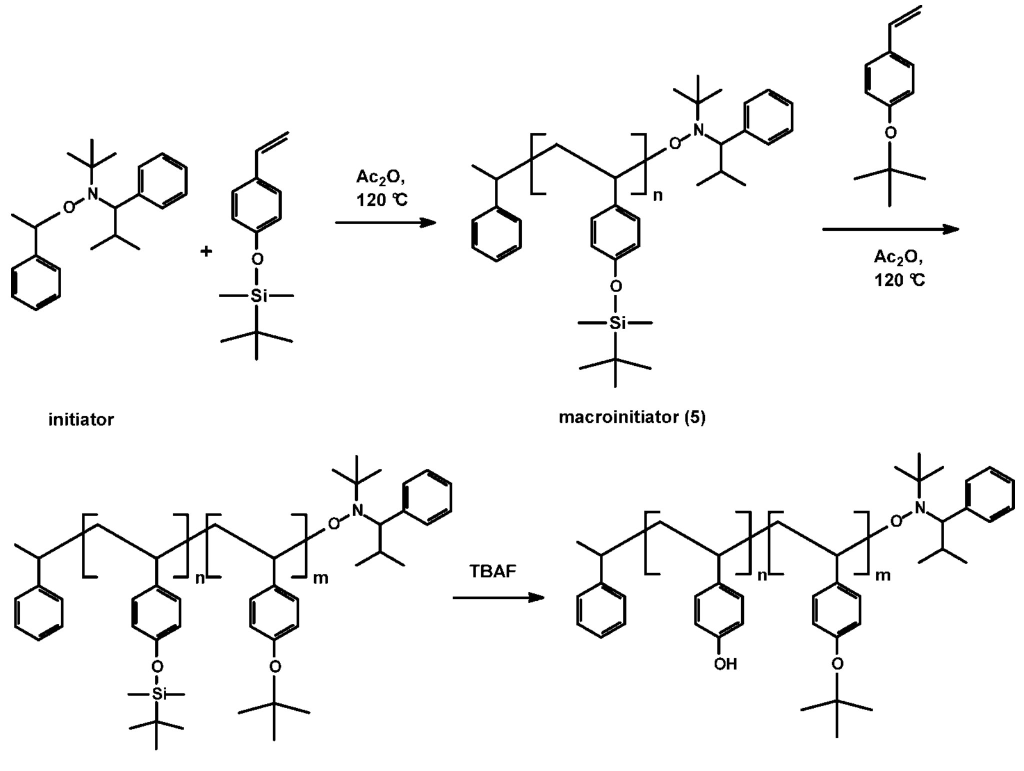


Figure 1. Partly *tert*-butoxycarbonyl (BOC; a) and *tert*-butoxy (TBU; b) protected block copolymers based on 4-hydroxystyrene with varying block ratios.

Scheme 1. Synthetic Approach for the Preparation of the Partly TBU Protected Block Copolymer P(H-OSt-*b*-TBU-OSt) 1:9 (30)



Ammonium chloride (≥99.5%), di-*tert*-butyldicarbonate (≥99.5%, Fluka), di-*tert*-butyl peroxide (98%, Aldrich), acetic anhydride (>99%, Aldrich), hydrazine monohydrate (98%, Aldrich), isobutyraldehyde (≥99%, Fluka), imidazole (99%, Aldrich), Jacobsen's catalyst (98%, Aldrich), sodium borohydride (≥96%, Fluka), potassium carbonate (water free, ≥99%, Fluka), 18-crown-6 (99%, Aldrich), Cu(II)acetate hydrate (≥98%, Aldrich), potassium hydroxide (≥86%, Fluka), 2-methyl-2-nitropropane (99%, Aldrich), sodium sulfate (water free, ≥99%, Fluka), phenylmagnesium chloride (1.8 M THF solution, Acros Organics), tetrabutylammonium fluoride (1 M THF solution, Aldrich), zinc powder (≥99%, Fluka), chloroform (>99%, Acros Organics), dichloromethane (≥99.8%, Merck), diethyl ether (≥99.8%, Fluka), ethyl acetate (>99.5%, Acros Organics), ethanol (technical grade, VWR Int.), *n*-hexane (≥99%, Merck), methanol (≥98.5%, VWR International), tetrahydrofuran (99.5%, Acros Organics), and toluene (99.5%, Acros Organics) were purchased and used without further purification.

2. Measurements. NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for ^{1}H and at 125.75 MHz for ^{13}C. Acetone-d_6 and $CDCl_3$ were used as solvents and internal standard ($\delta(^1H) = 2.05$ ppm, $\delta(^{13}C) = 30.5$ ppm and $\delta(^1H) = 7.26$ ppm, $\delta(^{13}C) = 77.0$ ppm, respectively). Signal assignments given in this paper were verified by ^{1}H−^{1}H shift correlated (COSY) spectra, ^{1}H−^{13}C heteronuclear multiple quantum correlation (HMQC) experiments, and ^{1}H−^{13}C heteronuclear

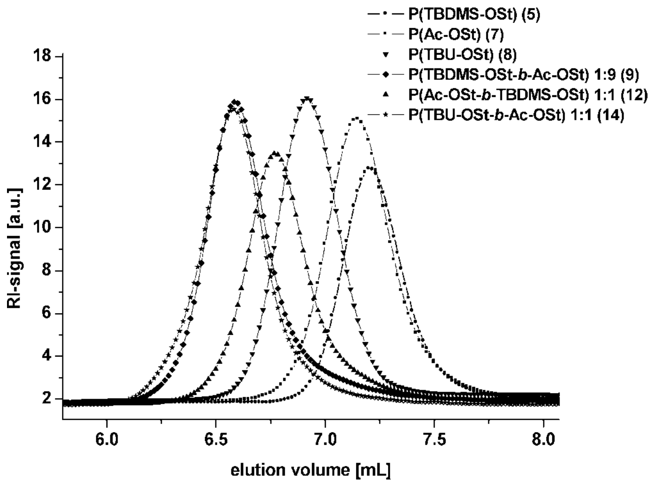


Figure 2. GPC curves of the macroinitiators P(TBDMS-OSt) (**5**), P(Ac-OSt) (**7**), P(TBU-OSt) (**8**), and their corresponding block copolymers P(TBDMS-OSt-*b*-Ac-OSt) 1:9 (**9**), P(Ac-OSt-*b*-TBDMS-OSt) 1:1 (**12**), and P(TBU-OSt-*b*-Ac-OSt) 1:1 (**14**) measured in $CHCl_3$ as eluent.

multiple bond correlation (HMBC) experiments. The pulse sequences included in the Bruker software package were used.

FT-IR spectra of the block copolymers were recorded on a Bruker IFS 66 V/S employing a Golden Gate ATR-unit from SPECAC (Kent/UK, crystal: diamond, single reflection, MCT detector). For each spectrum 100 scans were performed in the range between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. FT-IR spectra of the homopolymers were measured on a Bruker IPS 66 V/S in transmission mode using a DTGS detector. Spectra were recorded applying 32 scans in the range between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}.

Gel permeation chromatography (GPC) using narrow dispersed polystyrene standards (PL EasiCal PS-1, Polymer Laboratories) was used to determine molar masses and polydispersity indexes (PDI) of the polymers. GPC measurements with chloroform as eluent were performed applying a Polymer Laboratories PL Gel 10 μm mixed B column, a Knauer K-2301 RI detector, and a HPLC pump 64. For the GPC investigations with THF as eluent two PL Gel Mixed C columns (Polymer Laboratories), a Knauer RI detector and a HPLC pump were used. In all GPC measurements the flow rate was 1 mL/min.

Glass-transition temperatures (T_gs) were studied by a DSC Q1000 from TA Instruments with a scan rate of 20 K/min. All measurements were performed in a nitrogen atmosphere using aluminum capsules. For the determination of glass transition temperatures only the second heating cycles were applied using the half-step method.

Thermogravimetric investigations were performed using a TGA Q 500 from TA Instruments with a heating rate of 10 K/min in the temperature range between 30 and 700 °C. All experiments were run in a nitrogen atmosphere, and platinum pans were employed.

3. Monomer and Initiator Synthesis. The monomer 4-*tert*-butyldimethylsilyloxystyrene (TBDMS-OSt) was prepared as described in the literature, and the characterization data were in good agreement with the reported ones.[24]

Polymerization procedures via NMRP and the synthesis of the initiator 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane were performed similarly as described in the literature.[25–27]

Abbreviations of blocks as given in the polymer names: Ac-OSt = 4-acetoxystyrene; BOC-OSt = 4-*tert*-butoxycarbonyloxystyrene; H-OSt = 4-hydroxystyrene; TBDMS-OSt = 4-*tert*-butyldimethylsilyloxystyrene; TBU-OSt = 4-*tert*-butoxystyrene.

4. Synthesis Procedure of Macroinitiators via NMRP. General Procedure for P(TBDMS-OSt). In a round flask 3.20 g (13.6 mmol) of TBDMS-OSt together with 74.4 mg (0.2 mmol) of the initiator were introduced. Argon was bubbled through the solution for at least 15 min. The reaction mixture was then placed in a Schlenk tube, together with 51 mg (0.5 mmol) of acetic anhydride. Removal of traces of oxygen was performed by three freeze–pump–thaw cycles. The polymerization was started by immersing the Schlenk tube in a preheated oil bath (120 °C). After 16 h the polymerization was stopped by putting the Schlenk tube in a cold water bath. The colorless polymer was dissolved in 15 mL of chloroform and precipitated in 400 mL of ethanol. After repeating twice this procedure, the material was filtered off and dried under vacuum (40 °C) to constant weight. All polymers were obtained as white powders. Yields: P(TBDMS-OSt): 82% (**5**) (19 h), 96% (**6**) (16 h); P(Ac-OSt) (**7**): 94% (14 h); P(TBU-OSt) (**8**): 80% (14 h).

5. Synthesis of Precursor Block Copolymers. Synthesis of the Precursor Block Copolymer P(Ac-OSt-*b*-TBDMS-OSt) 1:1 (12) (General Procedure). In a round flask 1.51 g of macroinitiator poly(Ac-OSt) (**7**) together with 4.97 g (21.2 mmol) of TBDMS-OSt (**4**) were dissolved in 5 g of diglyme. Afterward an argon flow was bubbled through the solution in order to remove most of the oxygen. The reaction mixture was introduced in a Schlenk tube, and 40 mg (0.4 mmol) of acetic anhydride was then added. Traces of oxygen dissolved in the solution were removed by three freeze–pump–thaw cycles. The polymerization started after immersion the Schlenk tube in an oil bath preheated to 120 °C. After 24 h the tube was removed from the oil bath, and polymerization was stopped by cooling the Schlenk tube in a cold water bath. The highly viscous mixture was diluted with 12 mL of chloroform and precipitated in 500 mL of ethanol. This procedure was twice repeated in order to remove all traces of remaining monomer. The precipitated polymer was filtered off and dried at 40 °C to constant weight to give a white powder in 67% yield.

6. Synthesis of Target Block Copolymers via Orthogonal Polymer Analogous Reactions. *A. Removal of Acetyl Groups by Hydrazinolysis (Deacetylation) from Precursor Block Copolymer P(TBU-OSt-b-Ac-OSt) 1:1 (*14*) (General Procedure).* In a 1 L round flask 1.50 g of (5.3 mmol of acetyl groups) block copolymer P(TBU-OSt-*b*-Ac-OSt) 1:1 (**14**) were dissolved in 250 mL of dioxane. The solution was stirred for 15 min, and 1.5 mL (30 mmol) of hydrazine monohydrate was added slowly with a syringe. After ~20 min the solution became turbid. After additional stirring for 24 h the solution was concentrated, and then 5 mL of methanol was added in order to get a clear solution. The polymer was precipitated in 400 mL of water, filtered, and dried at 40 °C under vacuum. This procedure was repeated twice in order to remove all low molecular byproducts and impurities. After drying in high vacuum 1.245 g of P(TBU-OSt-*b*-H-OSt) 1:1 (**19**) was obtained as a white powder. According to ^1H NMR spectroscopy all acetyl groups have been quantitatively removed.

*B. Reprotection of the Free Phenolic OH Groups by tert-Butoxycarbonylation. Synthesis of P(TBDMS-OSt-b-BOC-OSt) 1:5 (*16*) (General Example).* In a 100 mL round flask 2.04 g (9.5 mmol of OH groups) of P(TBDMS-OSt-*b*-H-OSt) (**16**) was introduced. The polymer was dissolved in 30 mL of ethyl acetate, and afterward 3.31 g (23.9 mmol) of potassium carbonate (water free) and 2.65 g (12.2 mmol) of di-*tert*-butyl dicarbonate were added. The reaction mixture was stirred for 24 h at room temperature before the solids were filtered off. The filtrate was concentrated under reduced pressure, and the polymer was precipitated in 400 mL of methanol, filtrated, and dried under vacuum at 40 °C. The solid was again dissolved in ethyl acetate and precipitated in methanol. After filtration and drying under reduced pressure the polymer was obtained as a white powder. According to NMR analysis all OH groups were reprotected quantitatively by BOC protective groups.

*C. Desilylation with Tetrabutylammonium Fluoride (TBAF) Solution. Synthesis of P(H-OSt-b-BOC-OSt) 1:3 (*28*) (General Example).* In a 250 mL round flask 2.02 g (3.3 mmol TBDMS-groups) of P(TBDMS-OSt-*b*-BOC-OSt) 1:3 (**23**) was introduced. The polymer was then dissolved in 25 mL of THF(abs), followed by the addition of 7 mL of a 1 M TBAF solution (7 mmol). After 4 h of stirring the obtained red-brownish solution was concentrated under vacuum and precipitated in a water/methanol mixture (2:1 by volume), filtered, and dried under vacuum. The procedure was repeated twice, and finally the polymer was precipitated in *n*-hexane.

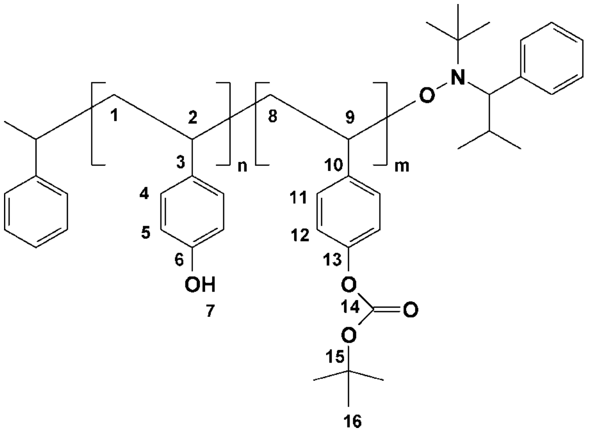
Table 1. Molar Masses, PDIs, and Conversions of the Synthesized Macroinitiators

macroinitiator	M_n [g/mol][a] (a) $CHCl_3$, (b) THF	$M_{n,cal}$[b] [g/mol]	PDI[a](a) $CHCl_3$, (b) THF	conversion[c] [%]
P(TBDMS-OSt) (**5**)	(a) 9100, (b) 10400	11900	(a) 1.16, (b) 1.13	82
P(TBDMS-OSt) (**6**)	(a) 8500, (b) 9500	13400	(a) 1.18, (b) 1.17	96
P(Ac-OSt) (**7**)	(a) 10400, (b) 8500	11900	(a) 1.22, (b) 1.20	94
P(TBU-OSt) (**8**)	(a) 20800, (b) 18900	23100	(a) 1.14, (b) 1.13	80

[a] Number- and weight-average molar masses and the polydispersity PDI = M_w/M_n were determined by GPC using (a) $CHCl_3$ and (b)THF as eluent. [b] Calculated molar mass: $M_{n,cal}$ = ([monomer]/[initiator]) × conversion × $M_{monomer}$. [c] Determined gravimetrically.

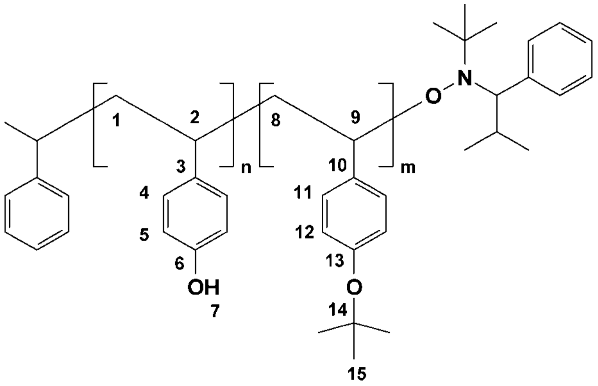
After filtration and drying to constant weight at 40 °C 1.32 g of a white powder was obtained. According to NMR analysis all TBDMS groups were quantitatively removed.

7. Characterization of Partly Protected Target Block Copolymers. *A. P(H-OSt-b-BOC-OSt) 1:9 (**26**), 1:5 (**27**), 1:3 (**28**).* ^{1}H NMR (acetone-d_6): δ (ppm) 8.1−7.7 (H-7), 7.15−6.3 (H-4, H-5, H-11, H-12), 2.4−1.75 (H-2, H-9), 1.75−1.2 (H-1, H-8), 1.53 (H-16). ^{13}C NMR (acetone-d_6): δ (ppm) 156.6 (C-6), 153.4 (C-14), 151.0 (C-13), 146.0−143.0 (C-10), 140.0−137.0 (C-3), 130.0 (C-4, C-11), 122.5 (C-12), 116.4 (C-5), 84.0 (C-15), 48.0−43.0 (C-1, C-8), 42.0−41.0 (C-2, C-9), 28.65 (C-16). FT-IR (cm^{-1}): 3345 (O−H), 3036 (aromat C−H), 2981 (aliphat C−H), 2928, 1886, 1753 (C=O), 1610 (Ar), 1507 (Ar), 1476, 1455, 1395, 1370, 1273, 1254, 1217, 1143, 1049, 1015, 893, 825, 782.



*B. P(BOC-OSt-b-H-OSt) 1:1 (**29**).* The ^{1}H and ^{13}C NMR spectra as well as the FT-IR spectra of P(BOC-OSt-*b*-H-OSt) (**29**) are analogous to those of the block copolymers P(H-OSt-*b*-BOC-OSt) (**26**), (**27**), and (**28**) just showing different signal intensities depending on the block ratio.

*C. P(H-OSt-b-TBU-OSt) 1:9 (**30**).* The partly protected polymer **30** was obtained by removal of the TBDMS protecting groups analogously to polymers **26**, **27**, **28**, and **29**.



^{1}H NMR (acetone-d_6): δ (ppm) 8.1−7.7 (H-7), 6.9−6.25 (H-4, H-5, H-11, H-12), 2.4−1.8 (H-2, H-9), 1.8−1.2 (H-1, H-8), 1.32 and 1.27 (H-15). ^{13}C NMR (acetone-d_6): δ (ppm) 156.6 (C-6), 155.0 (C-13), 144.0−140.0 (C-10), 140.0 – 137.0 (C-3), 131.0−128.0 (C-4, C-11), 125.0 (C-12), 116.4 (C-5), 78.8 (C-14), 49.0−43.0 (C-1, C-8), 42.0−40.0 (C-2, C-9), 30.0 (C-15). FT-IR (cm^{-1}): 3359 (O−H), 3028 (aromat C−H), 2975 (aliphat C−H), 2927, 1608 (Ar), 1579 (Ar), 1504 (Ar), 1474, 1449, 1388, 1363, 1300, 1235, 1160, 1104, 1015, 924, 897, 848, 833. Glass transition temperatures: $T_{g(1)}$ = 105 °C, $T_{g(2)}$ = could not be detected.

*D. P(TBU-OSt-b-OH-OSt) 1:1 (**19**).* The ^{1}H and ^{13}C NMR spectra as well as the FT-IR spectra of P(TBU-OSt-*b*-OH-OSt) 1:1 (**19**) are analogous to those of the block copolymer P(H-OSt-*b*-TBU-OSt) 1:9 (**30**) just showing different signal intensities depending on the block ratio. Glass transition temperatures: $T_{g(1)}$ = 110 °C, $T_{g(2)}$ = 186 °C.

Results and Discussion

The targeted partly protected block copolymers are shown in Figure 1. These 4-hydroxystyrene derivative materials were synthesized for the preparation of nanostructured films which should result from the self-assembly of the blocks with different polarity. The volume ratio of the different blocks is a very influencing factor[2,28] in terms of the formation of a special type of morphology in thin films. Therefore, the materials consist of blocks with different molar masses and different block ratios.

As already mentioned above protected 4-hydroxystyrene monomers can be polymerized in a controlled fashion by means of different radical polymerization techniques like NMRP, ATRP, and RAFT or by anionic polymerization. Because of unavoidable transfer reactions the direct radical polymerization of unprotected 4-hydroxystyrene provides polymers with very broad molecular weight distributions (MWD) and shows poor control over their molar masses.[29–32] Because of the protic phenolic OH groups the direct anionic polymerization of unprotected 4-hydroxystyrene is also not practicable. Therefore, only protected 4-hydroxystyrene monomers can be applied for anionic or controlled radical polymerization techniques.

Ito et al. have already prepared partially BOC protected block copolymers on the basis of 4-hydroxystyrene applying anionic polymerization and subsequent polymer analogous reactions.[33] Unfortunately, his approach required a high synthetic effort. Therefore, we favored a synthetic approach using a controlled radical polymerization technique like NMRP followed by a sequence of orthogonal and quantitative polymer analogous reactions.

Synthetic Strategy for the Preparation of Partly Protected Block Copolymers. Ohno et al.[34] have already shown that TBU protected 4-hydroxystyrene can be polymerized in a controlled fashion via NMRP. This indicates that the preparation of a poly(TBU-OSt) block in a diblock copolymer can be accomplished by the direct polymerization of the TBU protected monomer. The formation of the second block in the block copolymer requires another monomer possessing a protecting group which has to fulfill two important requirements. First, the protecting group has to be stable under the reaction conditions during NMRP, and second, this protecting group has to be orthogonally and quantitatively removable without affecting the TBU protecting groups.

According to the literature the acetyl group meets these requirements since acetyl protected 4-hydroxystyrene (4-acetoxystyrene) has already been successfully polymerized by NMRP, and the deprotection of the acetyl group can be performed by means of hydrazinolysis under neutral reaction conditions.[35,36] Another

Table 2. Synthesis of Precursor Block Copolymers from Different Macroinitiators via NMRP and Their Block Copolymer Characteristics

precursor block copolymer	macroinitiator $M_{n,cal}$[a] [g/mol]	M_n [g/mol][b] (a) $CHCl_3$, (b) THF	PDI[b](a) $CHCl_3$, (b) THF	$M_{n,cal}$[c] [g/mol]	percentage protecting groups[d] [mol %]
P(TBDMS-OSt-*b*-Ac-OSt) 1:9 (**9**)	P(TBDMS-OSt) (**5**) 11900	(a) 42900, (b) 52200	(a) 1.27, (b) 1.35	52100 (total) (11900 + 40200)	83.0 Ac, 17.0 TBDMS
P(TBDMS-OSt-*b*-Ac-OSt) 1:5 (**10**)	P(TBDMS-OSt) (**6**) 13400	(a) 26300, (b) 32100	(a) 1.25, (b) 1.23	37500 (total) (13400 + 24100)	72.2 Ac, 27.8 TBDMS
P(TBDMS-OSt-*b*-Ac-OSt) 1:3 (**11**)	P(TBDMS-OSt) (**6**) 13400	(a) 24800, (b) 21800	(a) 1.21, (b) 1.26	28700 (total) (13400 + 15300)	62.3 Ac, 37.7 TBDMS
P(Ac-OSt-*b*-TBDMS-OSt) 1:1 (**12**)	P(Ac-OSt) (**7**) 11900	(a) 27800, (b) 36100	(a) 1.24, (b) 1.31	40300 (total) (11900 + 28400)	37.7 Ac, 62.3 TBDMS
P(TBDMS-OSt-*b*-TBU-OSt) 1:9 (**13**)	P(TBDMS-OSt) (**5**) 11900	(a) 52700 (b) 70700	(a) 1.30, (b) 1.36	71800 (total) (11900 + 59900)	13.0 TBDMS, 87.0 TBU
P(TBU-OSt-*b*-Ac-OSt) 1:1 (**14**)	P(TBU-OSt) (**8**) 23100	(a) 48700, (b) 61900	(a) 1.26, (b) 1.32	53900 (total) (23100 + 30800)	59.2 Ac, 40.8 TBU

[a] Calculated molar mass: $M_{n,cal}$(macroinitiator) = ([monomer]/[initiator]) × conversion × $M_{monomer}$. [b] Number- and weight-average molar masses and the polydispersity PDI = M_w/M_n were determined by GPC using (a) $CHCl_3$ and (b) THF as eluent. [c] Calculated molar mass $M_{n,cal}$ of the precursor block copolymer was determined according to $M_{n,cal} = M_{n,cal}\text{(macroinitiator)} + [(n_2 \times M_2)/(n_1 \times M_1)] \times M_{n,cal}\text{(macroinitiator)}$, where n_1 = percentage protecting groups of macroinitiator block, n_2 = percentage protecting groups of second block, M_1 = molar mass of macroinitiator's monomer, and M_2 = molar mass of second block's monomer. [d] Percentage of protecting groups determined by ^1H NMR analysis.

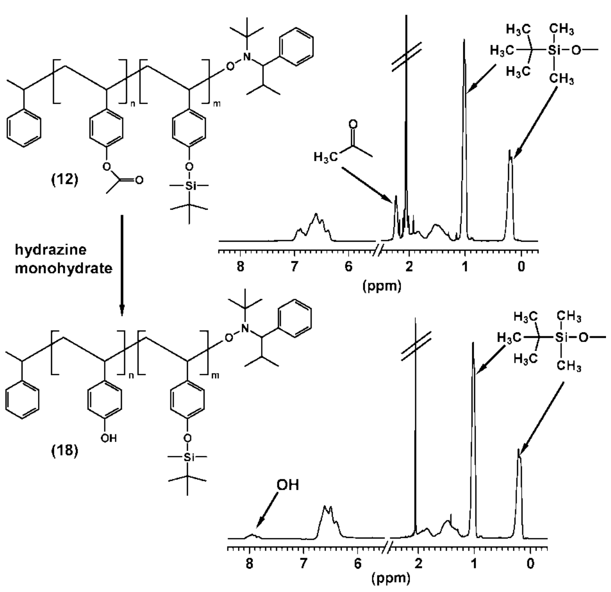


Figure 3. Orthogonal and quantitative removal of the acetyl groups in P(Ac-OSt-*b*-TBDMS-OSt) 1:1 (**12**) to provide P(H-OSt-*b*-TBDMS-OSt) 1:1 (**18**) proven by ^1H NMR characterization (solvent: acetone-d_6).

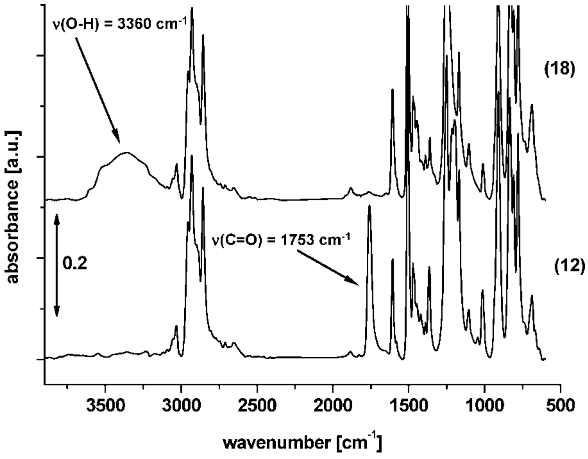
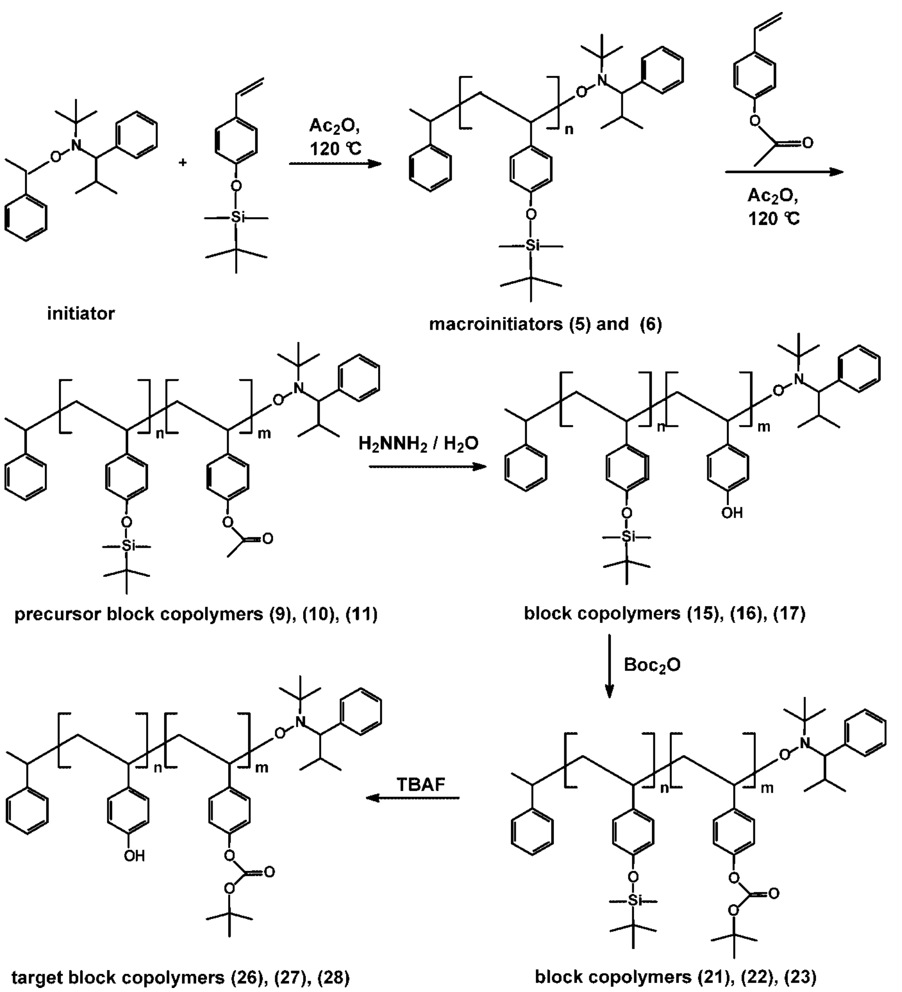


Figure 4. FT-IR spectra of the precursor block copolymers P(TBDMS-OSt-*b*-Ac-OSt) 1:1 (**12**) before and P(TBDMS-OSt-*b*-H-OSt) 1:1 (**18**) after hydrazinolysis.

promising monomer is a silyl protected 4-hydroxystyrene like 4-*tert*-butyldimethylsilyloxystyrene. The TBDMS protecting group should be stable under the conditions of NMRP and should be removable under relatively gentle reaction conditions by using TBAF.[37] As an example the synthetic approach for the preparation of the partly TBU protected block copolymer poly(4-hydroxystyrene-*b*-4-butoxystyrene) 1:9 (**30**) is shown in Scheme 1. Another possible approach for the preparation of a partly TBU protected block copolymer is to start with the preparation of a TBU protected macroinitiator poly(4-*tert*-butoxystyrene) (**8**) followed by the polymerization of Ac-OSt, which leads to the formation of an orthogonally protected block copolymer poly(4-*tert*-butoxystyrene-*b*-4-acetoxystyrene) (**14**). The removal of the acetyl groups by hydrazinolysis provides directly the partly protected target block copolymer poly(4-*tert*-butoxystyrene-*b*-4-hydroxystyrene) (**19**).

In contrast to the TBU protected 4-hydroxystyrene, the BOC protected monomer 4-*tert*-butoxycarbonyloxystyrene cannot be polymerized by NMRP due to thermal splitting of the BOC groups during the polymerization.[25] In order to synthesize partly BOC protected block copolymers, the synthetic strategy was modified as depicted in Scheme 2.

Scheme 2. Synthetic Strategy for the Preparation of Partly BOC Protected Target Block Copolymers P(H-OSt-*b*-BOC-OSt) 1:9 (26), 1:5 (27), and 1:3 (28)



It starts with the polymerization of a TBDMS protected 4-hydroxystyrene monomer to give a poly(4-*tert*-butyldimethylsilyloxystyrene) macroinitiator. The second block was synthesized by reinitiation of the macroinitiator in the presence of 4-acetoxystyrene. The acetyl groups of the formed precursor block copolymer poly(TBDMS-OSt-*b*-AcOSt) were removed by hydrazinolysis[38] using hydrazine monohydrate under neutral reaction conditions without affecting the TBDMS groups. Quantitative and orthogonal reprotection of the free phenolic hydroxyl groups was accomplished by means of *tert*-butylcarbonylation using di-*tert*-butyl dicarbonate under basic reaction conditions. This implies that the incorporation of the BOC protected repeating units in the block copolymers were performed by a polymer analogous reaction according to experiments already reported in the literature.[33,39] After the BOC groups were introduced into the polymer the deprotection of the TBDMS groups was accomplished by using tetrabutylammonium fluoride (TBAF).[33,39,40] The described polymer analogous reactions underwent orthogonally and quantitatively and most likely without substantial broadening of the molecular weight distribution (MWD) as described in previous references.[33,39] For the preparation of the target block copolymers P(H-OSt-*b*-BOC-OSt) 1:9 (**26**), 1:5 (**27**), and 1:3 (**28**) the TBDMS protected macroinitiators P(TBDMS-OSt) (**5**) and (**6**) were used while for the synthesis of P(BOC-OSt-*b*-H-OSt) 1:1 (**29**) the sequence of the block formation of the precursor block copolymer was reverse and the acetyl protected macroinitiator P(Ac-OSt) (**7**) was employed.

Synthesis and Characterization of Macroinitiators. For the synthesis of the macroinitiators by means of NMRP the alkoxyamine 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane was used as unimolecular initiator. An unimolecular system was chosen versus a bimolecular system (e.g., TEMPO/DBPO) as it allows best to obtain the desired molar masses much more easily than bimolecular systems. The preparation of the initiator was accomplished according to the literature in a three-step synthesis that was developed by Hawker et al.[25] 2.5 equiv of acetic anhydride with respect to the initiator was added as reaction accelerator. All polymerizations were carried out in bulk at 120 °C. They run for 14–19 h, and yields achieved were in the range between 80 and 96%. The homopolymers were precipitated in ethanol or methanol and were purified by several dissolution–reprecipitation cycles.

Molar masses and PDIs of the materials were determined by GPC using polystyrene (PS) standards. THF or $CHCl_3$ were used as eluents, and all obtained molar masses were in relatively good agreement with those calculated. PDIs are around 1.2, which is typical for NMRP with styrene derivatives. Deviations of the calculated molar masses of the macroinitiators and the measured molar masses are caused by the differences in the chemical structures of the polymers and polystyrene. However, GPC in the different solvents gave comparable results indicating that the macroinitiators interact similar to chloroform and THF, leading to similar hydrodynamic radii.

The GPC curves (Figure 2) of the synthesized macroinitiators are narrow and show a symmetric shape, indicating the formation of well-defined homopolymers. In principle, the molar masses of the polymers can also be calculated by end-group analysis using NMR spectroscopy. As every polymer chain should contain a nitroxide end group, the intensities of the signals of two terminal H atoms in the attached initiator fragments can be determined and molar masses can be calculated from that. As an example, for the macroinitiator P(TBDMS-OSt) (**5**) a molar mass of 18 200 g/mol was obtained by NMR end-group analysis compared to 13 500 g/mol, theoretically calculated. The very low intensities of the signals of the ends groups are most probably the origin for the discrepancy between the calculated molar masses and the molar masses determined by NMR end-group analysis, and this effect becomes even more dominant for higher molar mass polymers. Thus, no further end-group analysis data are presented.

Synthesis of Precursor Block Copolymers by NMRP. The synthesis of the macroinitiators could be accomplished in bulk due to the liquid nature of the monomers. But for the preparation of the block copolymers the added amount of monomer was not able to fully dissolve the solid macroinitiator, and therefore additional amount of solvent had to be added. An appropriate solvent was diglyme because it was able to dissolve the macroinitiators and the obtained precursor block copolymers as well. Moreover, the boiling point of diglyme is at 162 °C and significantly higher than the polymerization temperature (120 °C). For these reasons it was also previously chosen as a solvent for NMRP by other researchers.[41,42]

Since an increasing quantity of added solvent slows down the polymerization rate,[35] just the absolute necessary amount of diglyme was employed for the polymerizations. Furthermore, as for the synthesis of the macroinitiators, 2.5 equiv of acetic anhydride with respect to the initiator was added in order to accelerate the polymerization rate. Block copolymer formation took place by the incorporation of new monomer at the nitroxide terminated end of the polymer chains. The desired ratios of the blocks in the precursor block copolymers (Table 2) could be obtained by stopping the polymerization after a defined amount of monomer was consumed. Correlations between the reaction times and consumed amounts of monomer were evaluated in test polymerizations. Typically, polymerization rates of the precursor block copolymers were slower than those of the macroinitiators (homopolymers) due to the use of solvent. Therefore, longer reaction times of around 24 h were necessary in order to obtain yields in the range between 67 and 79%. Compositions of the precursor block copolymers were determined by integration of suitable peaks in the ^{1}H NMR spectra like the signals of the TBDMS groups, the acetyl groups, and the aromatic protons (Figure 3). The TBDMS groups provide two signals in the ^{1}H NMR spectra. One signal is at $\delta = 1.01$ ppm and caused by the *tert*-butyl groups, and the other one is located at $\delta = 0.21$ ppm and corresponds to the silylmethyl groups. The signals of the aromatic hydrogens are in the range between 7.1 and 6.3 ppm. The signal of the acetyl groups at $\delta = 2.23$ ppm was essential for the calculation of the composition in P(TBU-OSt-*b*-Ac-OSt) 1:1 (**14**). However, because of the small overlap with the broad signal of the methine protons, the accuracy of the calculation was slightly lower. The characteristics of the synthesized precursor block copolymers are summarized in Table 2.

Molecular weights and PDIs of the materials were determined by GPC measurements using $CHCl_3$ and THF as eluents. Here, the molar mass values determined in THF are consistently (with exception of (**11**)) higher than those determined in chloroform, indicating that THF is a better solvent for the second protected block. The PDIs of the precursor block copolymers were almost as low as those of the macroinitiators, indicating a good efficiency of the macroinitiators for reinitiation and block copolymer formation.

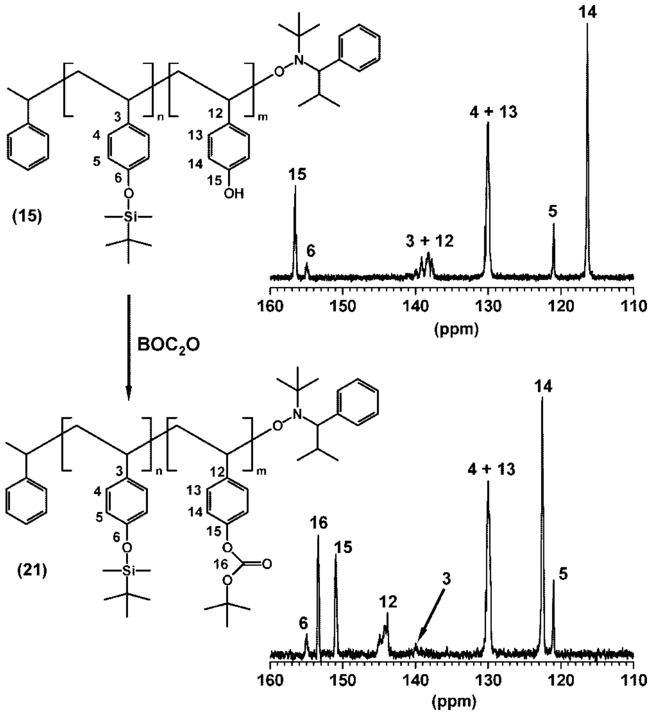


Figure 5. ^{13}C NMR spectra (aromatic carbons region) of P(TBDMS-OSt-*b*-H-OSt) 1:9 (**15**) and P(TBDMS-OSt-*b*-BOC-OSt) 1:9 (**21**) (solvent: acetone-d_6).

Synthesis of Partly Protected Block Copolymers by Polymer Analogous Reactions. As outlined above, the partly protected target block copolymers were synthesized by means of a sequence of orthogonal and quantitative polymer analogous reactions starting with the corresponding precursor block copolymers.

Deacetylation via Hydrazinolysis. The acetyl groups of the copolymers P(TBDMS-OSt-*b*-Ac-OSt) 1:9 (**9**), 1:5 (**10**), 1:3 (**11**), and P(Ac-OSt-*b*-TBDMS-OSt) 1:1 (**12**) were removed by hydrazinolysis under neutral conditions[38] which did not affect the TBDMS and TBU groups. Dioxane was used as solvent and a 6-fold excess of hydrazine monohydrate with respect to the acetyl groups of the polymers was employed. Under this reaction conditions, a quantitative and selective removal of the acetate groups could be observed. In Figure 3 the ^{1}H NMR spectrum of the precursor block copolymer P(Ac-OSt-*b*-TBDMS-OSt) 1:1 (**12**) and the spectrum of the obtained P(H-OSt-*b*-TBDMS-OSt) 1:1 (**18**) are depicted. While the signal of the acetyl groups appeared at 2.23 ppm for (**12**), it totally disappeared in the spectrum of the deprotected polymer (**18**). The unprotected phenolic OH groups gave rise to a broad signal in a range between 8.2 and 7.7 ppm. Since the solvent acetone-d_6 shows keto–enol tautomerism, a partial deuteration of the slightly acidic phenolic protons of the unprotected block occurred by H−D exchange, and therefore the signal caused by the phenolic OH groups could not be quantitatively analyzed.

The efficiency of the hydrazinolysis was also corroborated by FT-IR spectroscopy. In Figure 4 the FT-IR spectra of polymers **12** and **18** are shown. One can easily observe that the valence band of the carbonyl groups (Ac) of **12** at 1753 cm^{-1} completely disappeared in the spectrum of **18**. Instead, the broad band of the OH groups in the spectrum of **18** with a maximum at ca. 3360 cm^{-1} is clearly discernible.

Table 3. Molar Masses and PDIs of the BOC and TBDMS Protected Block Copolymers 21 to 24

partially BOC protected block copolymers (from: precursor)	M_n [g/mol][a] (a) $CHCl_3$, (b) THF	PDI[a] (a) $CHCl_3$, (b) THF	$M_{n,cal}$[b] [g/mol]
P(TBDMS-OSt-*b*-BOC-OSt) 1:9 (**21**) (from **15**[c])	(a) 55900, (b) 76400	(a) 1.39, (b) 1.65	66500 (total) (11900 + 54600)
P(TBDMS-OSt-*b*-BOC-OSt) 1:5 (**22**) (from: **16**[c])	(a) 29600, (b) 38000	(a) 1.30, (b) 1.30	46200 (total) (13400 + 32800)
P(TBDMS-OSt-*b*-BOC-OSt) 1:3 (**23**) (from: **17**[c])	(a) 24000, (b) 30700	(a) 1.26, (b) 1.27	34100 (total) (13400 + 20700)
P(BOC-OSt-*b*-TBDMS-OSt) 1:1 (**24**) (from: **18**[c])	(a) 29700, (b) 41400	(a) 1.21, (b) 1.20	44500 (total) (16100 + 28400)

[a] Number- and weight-average molar masses and polydispersity PDI = M_w/M_n were determined by GPC using (a) $CHCl_3$ and (b) THF as eluent. [b] Calculation of the molar mass of the partially BOC protected block copolymers was performed analogously like those of the precursor block copolymers (Table 2). [c] P(TBDMS-OSt-*b*-H-OSt) 1:9 (**15**), 1:5 (**16**), 1:3 (**17**), P(H-OSt-*b*-TBDMS-OSt) 1:1 (**18**).

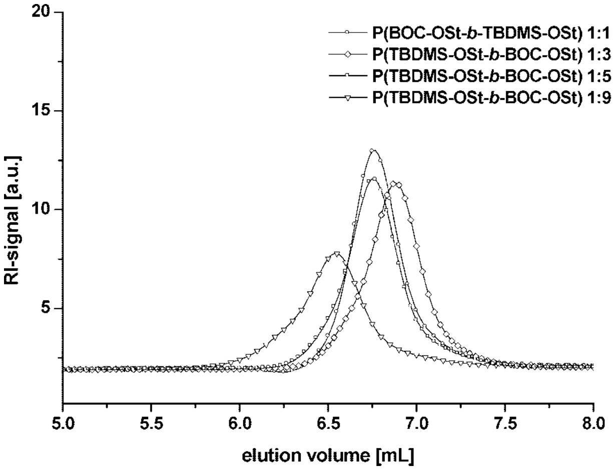


Figure 6. GPC curves of the BOC and TBDMS protected block copolymers P(TBDMS-OSt-*b*-BOC-OSt) 1:9 (**21**), 1:5 (**22**), 1:3 (**23**) and P(BOC-OSt-*b*-TBDMS-OSt) 1:1 (**24**) measured in $CHCl_3$ as eluent.

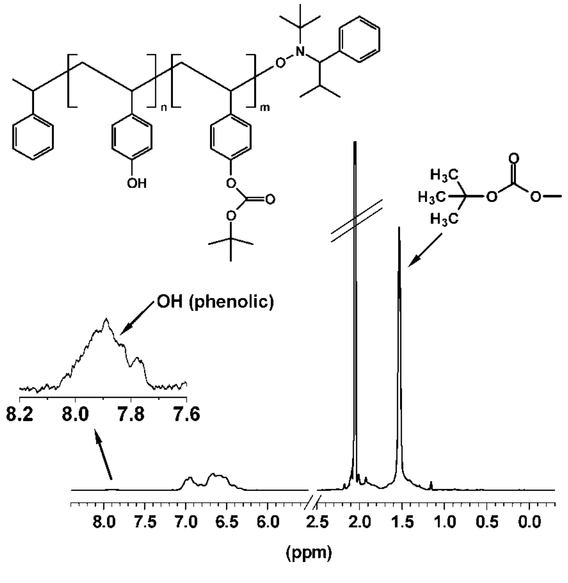


Figure 7. ^1H NMR spectrum of the target block copolymer P(H-OSt-*b*-BOC-OSt) 1:3 (**28**) (solvent: acetone-d_6).

Also, the deprotection of the acetyl groups in the precursor block copolymer P(TBU-OSt-*b*-Ac-OSt) 1:1 (**14**) proceeded quantitatively and orthogonally, providing P(TBU-OSt-*b*-H-OSt) 1:1 (**19**). In the ^1H NMR the signal of the acetyl group at δ = 2.23 pm (**14**) completely disappeared, whereas the signals of the TBU groups were not affected. In our case the determination of the molar masses of the partially protected block copolymers through GPC was not working due to the insolubility in $CHCl_3$, and when THF was used as eluent, partial irreversible adsorption of the polymers onto the column occurred, leading to unreliable results. Therefore, only the calculated molar masses ($M_{n,cal}$) of these polymers were reported in the following.

Reprotection of the Free Phenolic OH Groups by *tert*-Butoxycarbonylation. According to the synthetic approach outlined in Scheme 2, the free phenolic OH groups in the polymers P(TBDMS-OSt-*b*-H-OSt) 1:9 (**15**), 1:5 (**16**), 1:3 (**17**), and P(H-OSt-*b*-TBDMS-OSt) 1:1 (**18**) had to be reprotected by using di-*tert*-butyldicarbonate, as already described in the literature.[33,43] The quantitative reprotection of the phenolic OH groups could be unambiguously confirmed by comparing relevant signals in the corresponding ^{13}C NMR spectra of the educts and products. As an representative example, the aromatic carbons regions of the ^{13}C NMR spectra of P(TBDMS-OSt-*b*-H-OSt) 1:9 (**15**) and P(TBDMS-OSt-BOC-OSt) 1:9 (**21**) are presented in Figure 5 together with the reaction scheme.

One can clearly observe a significant shift of the signals of the aromatic C atoms C_{12}, C_{14}, and C_{15} in the ^{13}C NMR spectrum of **21** after the reprotection of the phenolic OH groups in **15**. Moreover, an intensive signal of the carbonyl group C_{16} at δ = 153.4 ppm is clearly discernible while the signals of the aromatic C atoms of the TBDMS protected block (C_3 to C_6) remained unchanged. Hence, the TBDMS protecting groups were not affected by the conditions and reagents of the *tert*-butoxycarbonylation reaction.

As for the precursor block copolymers and the macroinitiators, molar masses and polydispersities of **21** to **24** were determined by GPC using chloroform and THF as eluents. The obtained results are listed in Table 3.

Again, differences between the molar masses obtained by GPC and the corresponding calculated molar masses should arise from the use of polystyrene standards for calibration. The deviation of the molar masses obtained with THF and $CHCl_3$ as eluents were basically caused by a different hydrodynamic volume of the polymers in the elution media. Since the molar masses measured with THF as eluent are all higher than those obtained in $CHCl_3$, the solubility of the polymers **21** to **24** seems to be higher in THF. Nevertheless, determined PDIs with THF and $CHCl_3$ as eluents are quite similar and show values between 1.2 and 1.3 for the polymers **22**, **23**, and **24**. The GPC curves of the polymers **21** to **24** measured in $CHCl_3$ are depicted in Figure 6. In contrast to the GPC curves of **22**, **23**, and **24** the curve of **21** is not symmetrical, and its PDIs obtained in THF and chloroform are around 0.1 and 0.3 higher than those of the corresponding precursor block copolymer P(TBDMS-OSt-*b*-Ac-OSt) 1:9 (**9**). An explanation for the broadening of the molecular weight distribution in **21** and the tailing of the GPC curve might be that side reactions between different polymer chains occurred to a very small extent during hydrazinolysis of polymer **9**, leading to a covalent connection of different polymer chains. Similar observations have already been made by Chen et al.[38] However, the *tert*-butylcarbonylation reaction itself does not increase the molecular weight distributions as Ito et al. already reported.[33,39]

In the last step the removal of the TBDMS groups was performed using TBAF as a desilylation agent as already described by Corey et al.[37] and Ito et al.[33,40] The efficiency of this deprotection reaction could be proved by ^1H NMR analysis. In Figure 7 the ^1H NMR spectrum of the target block copolymer

Table 4. Calculated Molar Masses $M_{n,cal}$ of the Target Block Copolymers and the Calculated Molar Mass Ratios of the Unprotected and Protected Blocks

target block copolymer (from: precursor)	$M_{n,cal}$ [g/mol] unprotected block[a]	$M_{n,cal}$ [g/mol] protected block[a]	$M_{n,cal}$ [g/mol] (total)	molar mass ratio of the blocks
P(H-OSt-*b*-BOC-OSt) 1:9 (**26**) (from **21**)	6100	54600	60700	1:9
P(H-OSt-*b*-BOC-OSt)1:5 (**27**) (from **22**)	6900	32800	39700	1:4.7
P(H-OSt-*b*-BOC-OSt) 1:3 (**28**) (from **23**)	6900	20700	27600	1:3
P(BOC-OSt-*b*-H-OSt) 1:1 (**29**) (from **24**)	14600	16100	30700	1:1.1
P(TBU-OSt-*b*-H-OSt) 1:1 (**19**) (from **14**)	22800	23100	45900	1:1
P(H-OSt-*b*-TBU-OSt) 1:9 (**30**) (from **13**)	6100	59900	66000	1:9.8

[a] $M_{n,cal}$ of the blocks is based on the calculated molar masses of the corresponding precursor block copolymers Tables 2 and 3 considering a quantitative and orthogonal removal of the TBDMS or Ac protecting groups.

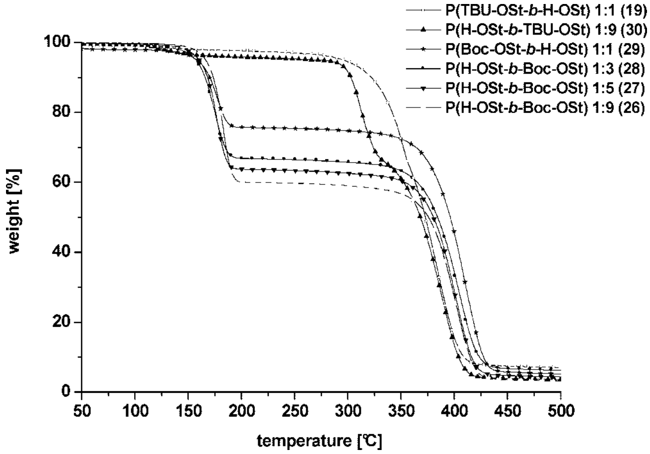


Figure 8. Thermogravimetric curves of the partly BOC and TBU protected target block copolymers (10 K/min heating rate in a nitrogen atmosphere).

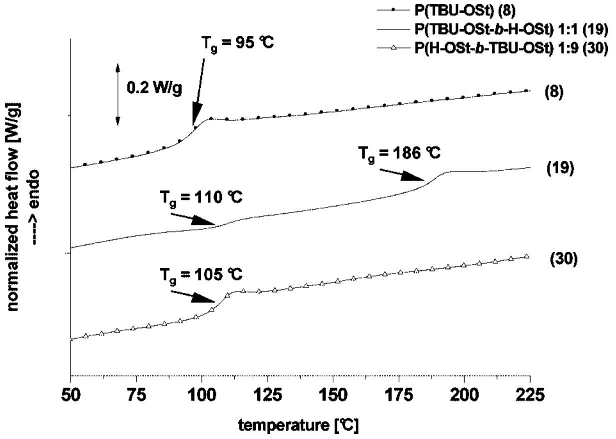


Figure 9. DSC curves and glass transition temperatures (determined via half-step method) of the macroinitiator P(TBU-OSt) (**8**) and the partly TBU protected block copolymers P(TBU-OSt-*b*-H-OSt) 1:1 (**19**) and P(H-OSt-*b*-TBU-OSt) 1:9 (**30**) (heating rate 20 K/min in a nitrogen atmosphere).

28 is shown after the removal of the TBDMS group from the block copolymer P(TBDMS-OSt-*b*-BOC-OSt) 1:3 (**23**).

The signals of the TBDMS group at $\delta = 1.02$ ppm and $\delta = 0.21$ ppm completely disappeared in the spectrum of P(H-OSt-*b*-BOC-OSt) 1:3 (**28**), and an additional signal between 8.1 and 7.7 ppm caused by the phenolic OH groups is clearly visible. Quantitative analysis of the ^{1}H NMR spectrum further showed that the intensity of the BOC groups signal at $\delta = 1.53$ ppm is not affected by the desilylation. Hence, the reaction proceeded orthogonally and quantitatively. This was also the case for the synthesis of the partly TBU protected target block copolymer P(H-OSt-*b*-TBU-OSt) 1:9 (**30**), applying the same reaction conditions like for the preparation of the partly BOC protected block copolymers.

Unfortunately, the partly TBU and BOC protected block copolymers adsorbed partly on the GPC column even when THF was used as eluent. Also using DMAc/LiCl as solvent for GPC did not improve the results. Therefore, a reliable determination of the molar masses and polydispersities of the target block copolymers via GPC was not possible. But according to Ito et al., the polydispersity of the polymers should not have been broadened by the desilylation reaction.[33,40] It is therefore very likely that the polydispersities of the target block copolymers are more or less the same like those of their corresponding precursor polymers. In Table 4, the calculated molar masses of the unprotected and protected blocks of the target block copolymers are listed together with block ratios.

Thermogravimetric Analysis. The thermal stability of the partly BOC and TBU protected block copolymers was investigated by thermogravimetric analysis (TGA). Recorded TGA thermograms are shown in Figure 8. The partly BOC protected block copolymers are characterized by two distinct thermal decomposition steps. The first decomposition process starts at ~130 °C arising from the loss of the BOC groups forming carbon dioxide and isobutylene. According to the literature, this process normally takes place for the homopolymer poly(4-*tert*-butoxycarbonyloxystyrene) at around 190 °C.[44,45] The removal of the BOC protecting groups in the homopolymer is just thermally induced. But in case of the block copolymers slightly acidic phenolic OH groups of the unprotected block are present, and an acid-catalyzed removal of the BOC groups takes place, leading to a start of the mass loss at already about 130 °C, which is finished at about 200 °C. This phenomenon has already been

Table 5. Comparison of the Calculated and Observed Mass Loss after Thermal Removal of the BOC Groups in the Partly BOC Protected Target Block Copolymers

partly BOC protected target block copolymer	calcd mass loss[a] [wt %]	obsd mass loss[b] [wt %]	T_{onset}[c] step 1 [°C]	T_{DTG}[c] step 1 [°C]	T_{onset}[c] step 2 [°C]	T_{DTG}[c] step 2 [°C]
P(H-OSt-*b*-BOC-OSt) 1:9 (**26**)	40.9	40.0	152	172	341	389
P(H-OSt-*b*-BOC-OSt) 1:5 (**27**)	37.5	36.4	150	164	331	378
P(H-OSt-*b*-BOC-OSt) 1:3 (**28**)	34.2	33.3	146	162	328	371
P(BOC-OSt-*b*-H-OSt) 1:1 (**29**)	23.9	24.5	143	159	330	375
P(H-OSt-*b*-TBU-OSt) 1:9 (**30**)		30.4	293	312	338	388
P(TBU-OSt-*b*-H-OSt) 1:1 (**19**)		34.2	322	351	350	384

[a] Calculated mass loss for complete removal of the BOC protecting groups based on the composition of target block copolymers determined by ^{1}H NMR analysis. [b] Mass loss at 200 °C determined from corresponding TGA thermogram. [c] Extrapolated onset (T_{onset}) and maximum (T_{DTG}) temperature determined from the derivative curves.

observed by Ito et al. for the randomly partly BOC protected poly(4-*tert*-butoxycarbonyloxystyrene-*ran*-4-hydroxystyrene).[45] Observed mass losses after the deprotection of the BOC groups in the target block copolymers are in good agreement with the calculated ones (Table 5).

By the removal of the BOC groups in the target block copolymers unprotected poly(4-hydroxystyrene) is formed which starts to degrade at an onset temperature of about 320 °C. Nicely, the phenolic OH-catalyzed thermal removal of the BOC protecting group opens a wider window for thermal deprotection without damaging the backbone structure. At around 450 °C this second decomposition process is finished, and only a few percent of the original weight of the target block copolymers is left over.

In comparison to the partly BOC protected block copolymers, the partly TBU protected block copolymers **19** and **30** are thermally much more stable and start to decompose just at about 285 °C. This process is most likely accompanied by a thermal induced removal of the *tert*-butyl protecting group which can be observed quite pronounced in the thermogram profile of the P(TBU-OSt-*b*-H-OSt) (**30**). The removal of the TBU groups is followed and maybe also partly overlapped by the degradation of the poly(4-hydroxystyrene) chains. Like for the partly BOC protected block copolymers the degradation processes are finished around 450 °C, and only a small amount of the block copolymers remained as a solid in the platinum pan.

Determination of Glass Transitions via Differential Scanning Calorimetry (DSC). Differential scanning calorimetry (DSC) experiments were performed for the partly TBU protected block copolymers **19** and **30** in order to elucidate phase separation in bulk. In Figure 9, the DSC curves of the block copolymers **19** and **30** are displayed together with that of the TBU protected homopolymer P(TBU-OSt) (**8**).

In the DSC thermogram of **19** two distinct glass transitions at 110 and at 186 °C are clearly discernible, indicating a phase-separated system. A comparison with the DSC curve of **8** suggests that the first glass transition at 110 °C is generated by a phase which consists mainly of the poly(TBU-OSt) blocks of **19**. The increase of glass transition temperature in **19** compared to that of **8** is most likely caused by an interaction of the P(TBU-OSt) and the unprotected P(H-OSt) blocks. According to the literature,[35] the second glass transition at 186 °C can be assigned to a phase that contains the unprotected P(H-OSt) chains. In case of target block copolymer **30** just one glass transition at 105 °C is observable. A second one could not be determined. This is maybe due to the fact that the amount of the unprotected blocks in **30** is much smaller that in **19**, and therefore the glass transitions is not pronounced enough to be seen in the DSC curve. But this does not necessarily mean that the system is not (at least) partly phase-separated.

Unfortunately, DSC analysis of of the BOC protected samples was not feasible due to the early thermal deprotection of the BOC groups and the accompanied significant mass loss which hampers DSC analysis. However, one can assume that a similar phase separation as observed for **19** occurs in the target block copolymers.

Conclusions

In conclusion, we have synthesized a family of partly *tert*-butoxycarbonyl (BOC) and *tert*-butyl (TBU) protected block copolymers based on poly(4-hydroxystyrene) possessing varying block ratios and molar masses. The method of choice for the preparation of orthogonally protected precursor block copolymers was NMRP applying acetyl (Ac), *tert*-butyldimethylsilyl (TBDMS), and TBU protected 4-hydroxystyrenes as monomers. Precursor block copolymers were synthesized by reinitiating presynthesized macroinitiators in the presence of an orthogonal protected monomer. All obtained precursor block copolymers show narrow polydispersity. Furthermore, a good control over the targeted molar masses and the ratios of the blocks in the block copolymers was accomplished. In order to obtain the desired target partly BOC and TBU protected block copolymers, a sequence of polymer analogous reactions was performed. For post polymer analogous modification reactions hydrazinolysis, *tert*-butoxycarbonylation and desilylation using TBAF were applied. These reactions proceeded orthogonally and quantitatively and most likely without a substantial increase of the polydispersity. Unfortunately, determination of the molar masses and PDIs of the target partly protected block copolymers via GPC was not feasible because of partial adsorption onto the GPC columns. Thermal stabilities were analyzed by TGA measurements and revealed in case of the partly BOC protected block copolymers a complete splitting of the BOC groups starting already at 130 °C since the phenolic groups catalyzed the deprotection. DSC investigations were also carried out for the partly TBU protected target block copolymers and evidenced a phase separated structure when the block ratio was nearly symmetrical.

For any potential use of these partially protected block copolymers in a hybrid patterning process, in a first step phase separation in thin films has to be achieved leading to patterns of a high order in the nanometer range. In a forthcoming paper, the phase separation behavior of the described block copolymers in thin films will be discussed in detail.[23]

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Supporting Information Available: NMR, FT-IR, and DSC characterization data of all block copolymers and macroinitiators. This information is available free of charge via the Internet at http://pub.acs.org.

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