Diblock Copolymers as Scaffolds for Efficient Functionalization via Click Chemistry

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ABSTRACT: A set of different alkyne containing diblock copolymers based on 4-hydroxystyrene was synthesized by nitroxide mediated radical polymerization (NMRP), all with excellent control over the molecular composition and narrow molar mass distribution. The diblock copolymers consist of labile protected 4-hydroxystyrene motifs in one block and bear alkyne functionalities in each repeating unit of the second block, thus making the materials candidates for polymer analogous modification reactions by a very efficient cycloaddition reaction. The use of 4-(trimethylsilylpropargyloxy)styrene as monomer proved highly advantageous compared to 4-(trimethylsilylethynyl) styrene, first because high control was kept in the NMRP process and second because there was higher accessibility in the postmodification reaction. In fact, quantitative postmodification through Cu(I)-catalyzed cycloaddition reaction of the pending propargyloxy groups with bulky adamantane azide of the diblock copolymers was achieved, yielding microphase-separated materials with a rigid block.

Introduction

During the past decade diblock copolymers have drawn high attention in the scientific world. Microphase separation of incompatible blocks leads to the formation of nanodimensioned features in the range 10−100 nm.[1] The size and ordering of these nanodomains can be controlled by varying the molecular weight, the chemical structure and the molecular architecture.[2] Although the mechanistic principles of the self-assembly of diblock copolymers in thin films are complex and not yet fully understood, scientists expect them to have a striking impact on nanotechnology.[3] The influence of surface effects in such thin films results in nanodomains that can be more complex and different from those being observed in bulk, i.e. spheres, cylinders, lamellae, etc.[4] State-of-the-art research is able to prepare highly oriented diblock copolymer thin films by different approaches.[5] Apart from their application in thin films, amphiphilic diblock copolymer micelles are used, e.g., as scaffolds for the preparation of cross-linked nanoparticles.[6]

Although, the polymers considered in the above-mentioned applications exhibit a high control over the molecular architecture, they are usually lacking defined functionalities, a fact that is directly related to ionic polymerization procedures by which most of the block copolymers investigated are currently synthesized. In order to satisfy the demand for complex and smart, further miniaturized devices in nanotechnology, new defined functional materials are required. This need can only be faced with novel methodologies. In this regard, controlled radical polymerizations (CRP) as NMRP,[7] ATRP,[8] and RAFT[9] are excellent tools for the preparation of such highly defined, functional block copolymers. They tolerate less rigorous reaction conditions and are compatible with a variety of functional groups so that these are nowadays preferred over ionic polymerization processes. Recently, Sharpless' click chemistry,[10] a Cu(I)-catalyzed version of Huisgen's 1,3-dipolar cycloaddition of azides and alkynes,[11] has been introduced in polymer science by various groups and recent comprehensive review articles can be found in literature.[12] Click chemistry adopted to polymer analogous reactions enables to efficiently and selectively tune the functionality and morphology of a polymeric material. Generally, suitable macromolecules can be considered as scaffolds and a large variety of polymers can be created from a construction kit of a plethora of reactive substrates. Remarkably, this concept had been suggested for polymer analogous modifications via pendant active esters some time ago.[13]

Specifically, segmented and "clickable" diblock copolymers would allow to manufacture nanodevices in which the functional domains could be selectively addressed in a click reaction and, thus, further modified. Only some examples for combinations of CRP and click chemistry should be depicted here from a research field which is rapidly expanding: Matjyaszewski's group[14] described the synthesis of poly(3-azidopropylmethacrylate-*b*-*N*,*N*-dimethylaminoethylmethacrylate) by ATRP and its polymer analogous modification with low molecular alkyne substrates. The obtained azido-functional polymers exhibited slightly broader SEC traces and, especially for high conversion, the polydispersity rose above 1.5, a fact that might be attributed to an in situ 1,3-dipolar cycloaddition reaction of the azide and the vinyl double bond of the monomer. Haddelton and coworkers[15] reverted to a well defined polymer based on propargyl methacrylate which they used as a scaffold for the preparation of synthetic glycopolymers by grafting azido−sugar derivatives along the polymer backbone. In their seminal work Hawker et al.[16] demonstrated the efficiency of click chemistry in polymer analogous modifications. They were able to orthogonally functionalize macromolecules in an one-pot synthesis using the strength of Cu(I)-catalyzed 1,3-dipolar cycloadditions and a couple of selected esterification as well as amidation reactions.

In this paper, we would like to report on the synthesis of reactive, phase-separated diblock copolymers that are prone to click chemistry as well as on first results on their effective polymer analogous modification with a bulky azide. On one hand, these macromolecules represent an ideal starting point for the modular synthesis of novel polymeric materials by effective side group modifications. On the other hand, potential applications of such diblock copolymers can be found in the fast developing field of nanostructured functional thin films. Recently, we could show that block copolymers based on 4-hydroxystyrene derivatives can be prepared in high molar masses and narrow polydispersity by nitroxide mediated radical polymerization (NMRP).[17,18] In particular, when one of the block consists of unprotected 4-hydroxystyrene, these block copolymers show a high tendency for phase separation, and thin films exhibiting a highly ordered nanostructure could be prepared.[19] By combining the phase separation tendency of that

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Table 1. Experimental Parameters and Analytical Data for the Macroinitiators MI-*x*

	protective group	n_{ini} [μmol]	$m_{monomer}$ [g]	conversion [%]	$M_{n,cal.}$ [g·mol^{-1}]	$M_{n,exp.}$ [g·mol^{-1}]	$M_{w,exp.}$ [g·mol^{-1}]	PDI
MI-1a	TBDMS	92.0	1.010	88	9700	7200	8400	1.16
MI-1b	TBDMS	280.0	5.005	70	12500	8600	9400	1.15
MI-2a	TBU	209	5.023	79	19800	15300	17500	1.15
MI-2b	TBU	88	6.125	85	50400	43700	52600	1.21
MI-2c	TBU	84	6.001	62	46400	41700	49600	1.19
MI-3	acetyl	139	4.960	58	20500	15800	20100	1.27

Table 2. Experimental Parameters for the Synthesis of Protected Precursor Diblock Copolymers

polymer	**MI**	n_{ini}[μmol]	$m_{\mathbf{6}}$ [g]	conversion [%]	$M_{n,cal.}$ [g·mol^{-1}]	$M_{n,exp.}$ [g·mol^{-1}]	$M_{w,exp.}$ [g·mol^{-1}]	PDI
pBC-1a	**MI-1a**	58	0.962	38	16 000	16 000	19 300	1.21
pBC-2a	**MI-2a**	25	1.011	48	36 000	26 300	31 900	1.21
pBC-2b	**MI-2b**	46	1.238	33	59 300	63 400	81 200	1.28
pBC-3	**MI-3**	49	1.060	49	31 100	24 400	33 700	1.38

Table 3. Experimental Parameters for the Synthesis of Precursor Diblock Copolymers with Random Distribution of the Alkyne Monomer 7 in the Second Block

polymer	**MI**	n_{ini} [μmol]	$m_{\mathbf{7}}$ [g]	$m_{styrene}$ [g]	conversion [%]	$M_{n,cal.}$ [g·mol^{-1}]	$w_{\mathbf{7}}{}^{a}$ [%]	$M_{n,exp.}$ [g·mol^{-1}]	PDI
pBC-1r	**MI-1b**	18	0.225	0.906	68	36 000	9	26 300	1.21
pBC-2r	**MI-2c**	60	0.392	2.002	48	66 400	13	62 400	1.34

[a] Amount of monomer **7** in the second block in mol %.

Table 4. Kinetic Experiment for the Cu(I)-Catalyzed Addition of 1-Adamantane Azide to HP-6 and HP-7

polymer	$m_{polymer}$ [mg]	n_{alkin} [μmol]	n_{azide} [μmol]	$m_{Cu\text{-}cat.}$ [mg]	m_{DIPEA} [mg]	conversion [%]
A-HP-6	99.9	631	672	51.6	240.3	100
A-HP-7	77.5	605	648	54.7	242.9	75

type of block copolymers with effective side group modification, it should be possible to create thin microphase-separated films where nanoscopic domains might be exclusively addressed by orthogonal reaction techniques.

Experimental Part

Chemicals. THF (99%, Fluka) and acetone (99.5%, Merck) were used as received, and dichloromethane (DCM, 99%, Fluka), triethylamine (99.5%, Fluka), diisopropylethylamine (DIPEA, 99%, Aldrich), diazabicycloundecene (DBU, 97.5%, Aldrich), and diethylene glycol dimethylether (diglyme, 99%, Aldrich) were dried over CaH_2 and purified by fractionated distillation. The synthesis of 4-(*tert*-butyldimethylsilyloxy)styrene[21] (**1**) was described elsewhere and the monomers 4-(*tert*-butyloxy)styrene (**2**, TBU−oxystyrene, 99%, Aldrich) and 4-acetoxystyrene (**3**, 96%, Aldrich) were distilled before use. All other reagents and solvents were purchased from Aldrich and used as received. *N-tert*-Butyl-α-isopropyl-α-phenylnitroxide (**TIPNO**), 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (initiator, **TIPNO-Sty**), and $Cu(PPh_3)_3Br$ were synthesized as described elsewhere.[20] Tetrabutylammonium fluoride [(TBA)F] was available from Aldrich as a 1 M solution in THF containing 5% water. Adamantane azide (97%) was used as received from Aldrich.

Measurements. Molar masses and polydispersities of polymer samples were determined by gel permeation chromatography (GPC) using a 10 μm MIXED-B column (Polymer Laboratories) with polystyrene standards (Polyscience) and chloroform as eluent. ^{1}H and ^{13}C measurements were performed with a Bruker DRX 500 spectrometer. $CDCl_3$ and acetone-d_6 were used as solvents and internal standard ($\delta(^1H) = 7.26$ ppm, $\delta(^{13}C) = 77.0$ ppm and $\delta(^1H) = 2.05$ ppm, $\delta(^{13}C) = 30.5$ ppm, respectively). Signal assignments were verified by 2D NMR experiments. The pulse sequences included in the Bruker software package were used.

All FT-IR spectra were recorded from prepared films in transmission mode on a Bruker IFS 66 V/S. Differential scanning calorimetry (DSC) was preformed with a DSC 7 from Perkin-Elmer as well as a DSC Q 1000 by TA Instruments with a heating rate of 20 K/min. The TGA analyses were conducted with a TGA 7 by Perkin-Elmer under nitrogen atmosphere with a heating rate of 10 K/min.

Monomer Synthesis. *4-Hydroxystyrene (**4**).* The synthesis and characterization can be found in the Supporting Information.

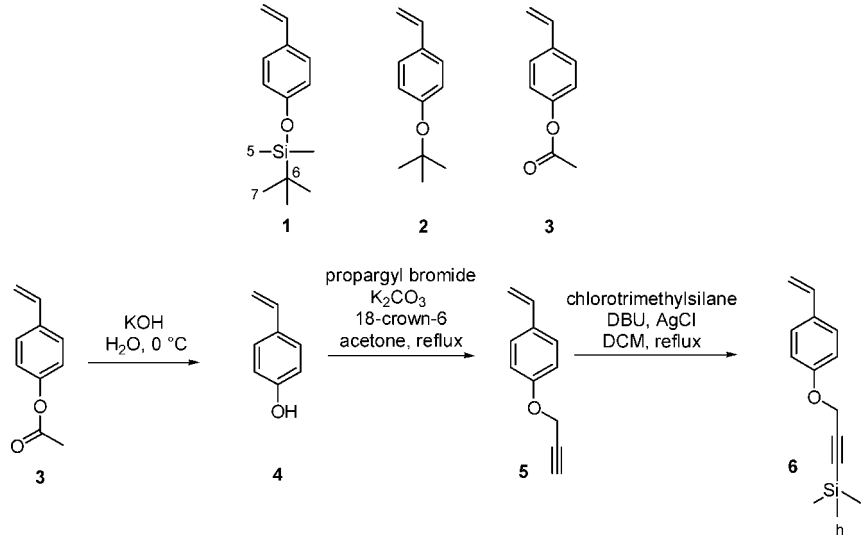
*4-(Propargyloxy)styrene (**5**).* A 250 mL round-bottom flask, equipped with a condenser and a stirrer, was fed with 6.90 g (57 mmol) of freshly prepared 4-hydroxystyrene (**4**), dissolved in 50 mL of acetone. Then, 26.06 g (116 mmol) of potassium carbonate and 1.87 g (11 mmol) of 18-crown-6 were dispersed. The mixture was heated to reflux and 13.38 g (89 mmol) of propargyl bromide (80% in toluene) was added. The reaction was kept under nitrogen atmosphere. After 20 h the product was precipitated into 300 mL of deionized water and 80 mL of chloroform was added. The organic phase was separated, and the water phase was extracted three times with 80 mL of chloroform used each time. The organic layers were combined, dried over sodium sulfate, and evaporated. The crude product was purified by flash chromatography using *n*-hexane and ethyl acetate (100:1) as solvent resulting in 5.54 g (61%) of a colorless liquid.

^{1}H NMR ($CDCl_3$): δ = 7.38 (d, H_b), 6.96 (d, H_c), 6.69 (dd, C*H*=CH_2), 5.65 (d, CH=C$H_{2,trans}$), 5.17 (d, CH=C$H_{2,cis}$), 4.70 (d, H_e), 2.54 ppm (t, H_g). ^{13}C NMR ($CDCl_3$): δ = 157.25 (C_d), 136.06 (*C*H=CH_2), 131.31 (C_a), 127.34 (C_b), 114.91 (C_c), 112.04 (CH=*C*H_2), 78.49 (C_f), 75.52 (C_g), 55.80 ppm (C_e).

*4-(3′-Trimethylsilylpropargyloxy)styrene (**6**).* A 100 mL 2-neck round-bottom protection flask, equipped with a condenser and a dropping funnel, was dried in a high vacuum at 350 °C. Under a nitrogen atmosphere, 538 mg (4 mmol) of silver chloride was dispersed in 30 mL of dry dichloromethane and 5.54 g (35 mmol) of 4-(propargyloxy)styrene (**5**) and 6.50 g (43 mmol) DBU were added. The suspension was heated under reflux and 4.90 g (45 mmol) trimethylsilyl chloride were dropped slowly. After 18 h, complete conversion of the free alkyne was indicated by TLC so that the reaction mixture was cooled to room temperature and diluted with 60 mL hexane. The crude product was washed with a semiconcentrated sodium hydrogen carbonate solution and with 1% HCl. The organic layer was removed, dried over sodium sulfate and evaporated. The product was isolated by column chromatography over silica gel with *n*-hexane and ethyl acetate (100:1) as solvent resulting in 3.38 g (42%) of a colorless oil.

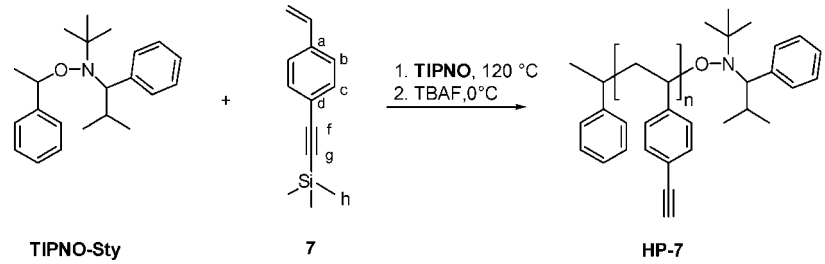
^{1}H NMR ($CDCl_3$): δ = 7.35 (d, H_b), 6.93 (d, H_c), 6.67 (dd, C*H*=CH_2), 5.62 (d, CH=C$H_{2,trans}$), 5.14 (d, CH=C$H_{2,cis}$), 4.68 (s, H_e), 0.18 ppm (s, H_h). ^{13}C NMR ($CDCl_3$): δ = 157.59 (C_d), 136.15 (*C*H=CH_2), 131.16 (C_a), 127.28 (C_b), 115.01 (C_c), 111.93

Scheme 1. Overview on the Monomers Used for the Syntheses of Diblock Copolymers[a]



[a] The synthetic route to the alkyne monomer 4-(3′-trimethylsilylpropargyloxy)styrene (**6**) involves a straightforward three step synthesis.

Scheme 2. Polymerization of 7 by NMRP Resulting in MI-7 That Was Subsequently Desilylated To Yield HP-7[a]



[a] In analogy, **6** was polymerized to **MI-6** (without **TIPNO**) and desilylated to **HP-6**.

(CH=CH_2), 100.02 (C_f), 92.78 (C_g), 56.81 (C_e), −0.31 ppm (C_h). IR (KBr): 3088−3041 (Ar−H) (w), 2960−2900 (C−H) (s), 2179 (C≡C) (w), 1606 (C_{Ar}=C_{Ar}) (m), 1510 (C_{Ar}=C_{Ar}) (s), 1251 (Ar−O−C) (s).

*4-(Trimethylsilylethynyl)styrene (***7***).* **7** was synthesized via a Sonogashira reaction from 4-bromostyrene as described elsewhere.[23] ^{1}H NMR ($CDCl_3$): δ = 7.43 (d, H_b), 7.34 (d, H_c), 6.69 (dd, C*H*=CH_2), 5.76 (d, CH=C$H_{2,trans}$), 5.29 (d, CH=C$H_{2,cis}$), 0.26 ppm (s, H_g). ^{13}C NMR ($CDCl_3$): δ = 137.65 (C_a), 136.24 (*C*H=CH_2), 132.14 (C_c), 126.01 (C_b), 122.41 (C_d), 114.80 (CH=*C*H_2), 105.11 (C_f), 94.81 (C_g), −0.03 ppm (C_h).

Polymer Synthesis. All polymerizations were carried out in Schlenk tubes under nitrogen atmosphere at 120 °C in bulk. Macroinitiators and diblock copolymers of different molecular weights $M_{n,cal}$ and block ratios, respectively, were obtained by changing the initiator to monomer ratio taking into account the degree of conversion α: i.e., $n_{ini} = \alpha * m_{monomer}/M_{n,cal}$. Reaction solutions were all degassed by four freeze−pump−thaw cycles prior to polymerization. The polymerizations were stopped by cooling in an ice-cold bath. If not mentioned else, the samples were precipitated twice in ethanol and dried at 50 °C in high vacuum overnight.

Synthesis of Macroinitiators (MI-x). A detailed description of the macroinitiator syntheses can be found in our previous paper.[18] Information about the characterization is provided in the Supporting Information.

Synthesis of the Alkyne-Containing Homopolymers **HP-6** *and* **HP-7***. Poly(TMSpropargyloxystyrene) (***MI-6***).* The general polymerization procedure as described above was applied. Initially, the Schlenk tube was carefully cleaned by repeated washing with water and acetone, thereafter flame dried in high vacuum to remove moisture and purged with nitrogen. Then, a solution of 85.4 mg (284 μmol) of initiator **TIPNO-Sty** in 3.5447 g (15 mmol) **6** was prepared in a vial, transferred in the Schlenk tube, degassed and polymerized. After 16 h the reaction was stopped and the polymer worked up. After drying, 1.630 g (46%) polymer could be isolated.

^{1}H NMR ($CDCl_3$): δ = 6.8−6.2 ($H_{b,c}$), 4.59 (H_e), 2.1−1.5 (CH), 1.5−1.1 (CH_2), 0.18 ppm (H_h). ^{13}C NMR ($CDCl_3$): δ =

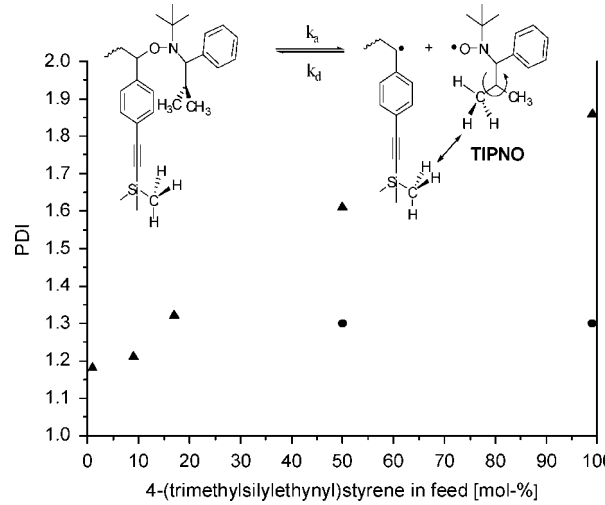


Figure 1. Influence of the feed composition for a copolymerization of styrene and **7** on the PDI with (•) and without (▲) addition of free nitroxide **TIPNO**.

Table 5. Experimental Parameters and Analytical Data for the Silyl-Protected Model Polymers MI-6 and MI-7

polymer no.	n_{ini}[μmol]	n_{TIPNO} [μmol]	$m_{monomer}$ [g]	conversion [%]	$M_{n,cal}$ [g·mol^{-1}]	$M_{n,exp}$ [g·mol^{-1}]	PDI
MI-6a	29	0	461.1	81	12400	12900	1.31
MI-6b	284	0	3.545	46	6600	6200	1.23
MI-7a	334	408	2.854	67	5700	3400	1.23
MI-7b	439	0	1.812	88	36200	28100	1.86

155.8 (C_d), 139.5−137.0 (C_a), 128.3 (C_b), 114.4 (C_c), 100.6 (C_f), 92.2 (C_g), 56.9 (C_e), 47.0−41.0 (CH_2), 39.4 (CH), −0.22 ppm (C_h). GPC ($CHCl_3$): M_n = 5200 g/mol, M_w = 6400 g/mol, PDI = 1.23. DSC: T_g = 48 °C. FT-IR (ATR): ν = 3026 (C_{ar}−H), 2912 (C_{ali}−H), 2324, 2178, 2051, 1609 (C_{ar}−C_{ar}), 1507, 1449, 1363, 1303, 1214, 1176, 1114, 1037, 833 cm^{-1}.

*Poly(propargyloxystyrene) (***HP-6***).* A solution of 1.1652 g of **MI-6** in THF was reacted with 5 mL of 1 M (TBA)F solution at 0 °C for 30 min. The product was recovered by precipitation from ethanol in 80% yield.

^{1}H NMR ($CDCl_3$): δ = 7.0−6.2 ($H_{b,c}$), 4.63 (H_e), 2.50 (H_g), 2.2−1.6 (CH), 1.6−1.1 ppm (CH_2). ^{13}C NMR ($CDCl_3$): δ = 155.4 (C_d), 139.5−137.0 (C_a), 128.3 (C_b), 114.3 (C_c), 78.8 (C_f), 75.4 (C_g), 55.8 (C_e), 47.0−41.01 (CH_2), 39.5 ppm (CH). GPC ($CHCl_3$): M_n = 3100 g/mol, M_w = 4000 g/mol, PDI = 1.29. DSC: T_g = 54 °C. FT-IR (ATR): ν = 3282 (C_{alkyne}−H), 3031 (C_{ar}−H), 2920 (C_{ali}−H), 2324, 2178, 2051, 1749 (C═O), 1608 (C_{ar}−C_{ar}), 1504, 1446, 1366, 1187, 1014, 911, 829 cm^{-1}.

*Poly(ethynylstyrene) (***HP-7***).* This was synthesized according to a procedure developed previously in our laboratory.[24] More details on synthesis and characterization can be found in the Supporting Information.

GPC ($CHCl_3$): M_n = 2200 g/mol, M_w = 2800 g/mol, PDI = 1.27, M_n(^{1}H NMR) = 2600 g/mol, M_n(cal) = 2600 g/mol. DSC: T_g = 153 °C.

General Procedure for the Synthesis of the Precursor Diblock Copolymers pBC-x. The macroinitiators **MI-*x*** were dissolved in a minimum amount of diglyme and comonomer **6** was added to the solution. The mol number of initiator needed to obtain the diblock copolymer of a desired block ratio was calculated as described above based on $M_{n,cal.}$ of the macroinitiator (Table 2). As an example, in a vial, 566.1 mg (58 μmol) of **MI-1a** was completely dissolved in 962.2 mg (4.2 mmol) of **6** and 0.5 mL of diglyme. Thereafter, the solution was transferred in a Schlenk tube, degassed, and polymerized at 120 °C under nitrogen atmosphere. After 18 h, the reaction was stopped by cooling, and 0.535 g (35%) of polymer was isolated by repeated precipitation in methanol.

In case of the syntheses of precursor diblock copolymers in which the alkyne monomer **7** is randomly distributed in the second block with styrene, the same methodology was followed (Tables 3 and 4).

The ^{1}H NMR, ^{13}C NMR, IR, DSC, and TGA data can be found in the Supporting Information.

General Procedure for the Synthesis of the Target Diblock Copolymers **BC-x**. The silyl-protected precursor diblock copolymers **pBC-*x*** were selectively desilylated by an excess tetrabutylammonium fluoride [(TBA)F] at 0 °C using THF as solvent. As an example, 502.1 mg of silyl-protected diblock copolymer **pBC-1a** was dissolved in 10 mL of THF and cooled at 0 °C, and 2.2 mL of a 1 M solution of (TBA)F in THF was slowly added by a syringe. After 1 h of stirring at 0 °C, the solution was reduced in a vacuum, and the residue was precipitated in ethanol twice. After drying in a high vacuum at 50 °C overnight, 201 mg (67%) of a solid product was recovered. Be aware that by that procedure the TBDMS protecting group was also removed in the respective block copolymers (e.g., **BC-1**).

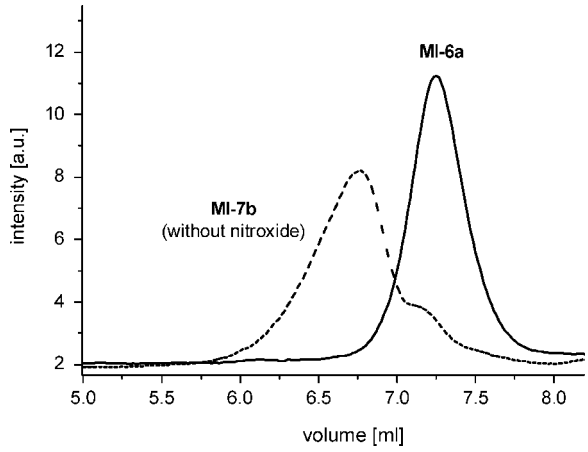


Figure 2. SEC traces of the homopolymers **MI-7b** and **MI-6a**.

The ^{1}H NMR, ^{13}C NMR, IR, DSC, and TGA data can be found in the Supporting Information.

General Procedure for the Polymer Analogous Click Reactions. All click reactions were performed in Schlenk tubes at room temperature using THF or $CDCl_3$, respectively, as solvent. No precautions were undertaken to exclude oxygen or moisture. As catalyst $Cu(PPh_3)_3Br$ was used in 0.1 equivalents and DIPEA in 3-fold excess, with respect to pendent alkyne groups. The reactions were stopped after full conversion for **HP-6** was achieved as determined by ^{1}H NMR spectroscopy.

*Poly(4-(1′-adamantanyltriazolylmethyloxy)styrene) (***A-HP-6***) and Poly(4-(1′-adamantanyltriazolyl)styrene) (***A-HP-7***).* The reactions were carried out in $CDCl_3$ at 40 °C. Samples were taken and the conversion was monitored by ^{1}H NMR spectroscopy. The final products were worked up by repeated precipitation from acetonitrile.

A-HP-6. ^{1}H NMR ($CDCl_3$): δ = 7.9−7.7 (H_g'), 7.0−6.2 ($H_{b',c}'$), 5.1 (H_e'), 2.21 ($H_{8,9}$), 2.2−1.0 (CH and CH_2), 1.76 ppm (H_{10}). ^{13}C NMR ($CDCl_3$): δ = 156.4 (C_d'), 143.1 (C_f'), 140.0−137.0 (C_a'), 128.6 (C_b'), 119.8 (C_g'), 114.2 (C_c'), 62.2 (C_e'), 59.7 (C_7), 46−38 (CH and CH_2), 42.9 (C_8), 39.7 (*C*H), 35.9 (C_{10}), 29.4 ppm (C_9). DSC: T_g = 168 °C.

A-HP-7. ^{1}H NMR ($CDCl_3$): δ = 8.2−6.2 ($H_{b',c',b,c,g}'$), 2.99 (H_f), 2.28 ($H_{8,9}$), 1.18 (H_{10}), 2.5−1.1 ppm (CH and CH_2). ^{13}C NMR ($CDCl_3$): δ = 146.8 (C_f'), 146−143 ($C_{a',a}$), 132.5 −131.0 (C_c), 130−126 (C_b',$_{d',b}$), 126.0−124.5 (C_c'), 120.0−118.5 (C_d), 117.5−115.5 (C_g'), 84.0 (C_f), 77.6 (C_g), 59.5 (C_7), 46−38 (CH and CH_2), 42.9 (C_8), 36.0 (C_{10}), 29.5 ppm (C_9). Signals of ethynylstryrene were observed because of only ∼75% final conversion. Except for signals due to the adamantanyl moiety (7−10 ppm), all signals were strongly broadened by restricted mobility of the polymer backbone. DSC: T_g could not be observed below the decomposition temperature.

Poly(TBU-oxystyrene-*b*-4-(1′-adamantanyltriazolylmethyloxy)-styrene) (A-BC-2b). A solution of 204.5 mg (155 μmol) of poly(*tert*-butyloxystyrene)-*block*-poly(propargyloxystyrene) (**BC-2b**) in 10 mL of THF was prepared and 19.0 mg (20 μmol) of $Cu(PPh_3)_3Br$ and 55.5 mg (429 μmol) of DIPEA as well as 94.7 mg (530 μmol) of 1-adamantane azide were added. The reaction mixture was stirred for 48 h at 50 °C. The product was worked up by repeated precipitation from acetonitrile in 67% yield.

^{1}H NMR ($CDCl_3$): δ = 7.81 (H_g'), 6.8−6.5 ($H_{3,b',c}'$), 6.5−6.3 (H_2), 5.07 (H_e'), 2.21 ($H_{8,9}$), 2.2 −1.2 (CH and CH_2), 1.76 (H_{10}), 1.26 ppm (H_6). ^{13}C NMR ($CDCl_3$): δ = 156.4 (C_d'), 152.9 (C_4), 143.1 (C_f'), 141.5−139.0 (C_1), 139.0−137.0 (C_a'), 129.0−127.0 ($C_{2,b}'$), 123.6 (C_3), 119.6 (C_g'), 114.1 (C_c'), 77.7 (C_5), 62.2 (C_e'), 59.5 (C_7), 47.5−42.0 (CH_2), 42.9 (C_8), 39.7 (CH), 35.9 (C_{10}), 29.4 (C_9), 28.9 ppm (C_6). GPC ($CHCl_3$): M_n = 54 100 g/mol, M_w = 64 900 g/mol, PDI = 1.20. DSC: T_g = 105 °C. FT-IR (ATR): ν = 3026 (C_{ar}−H), 2974, 2911 (C_{ali}−H), 2324, 2164, 2086, 1981, 1607 (C_{ar}−C_{ar}), 1504, 1451, 1388, 1256, 1160, 1086, 1013, 924, 849 cm^{-1}.

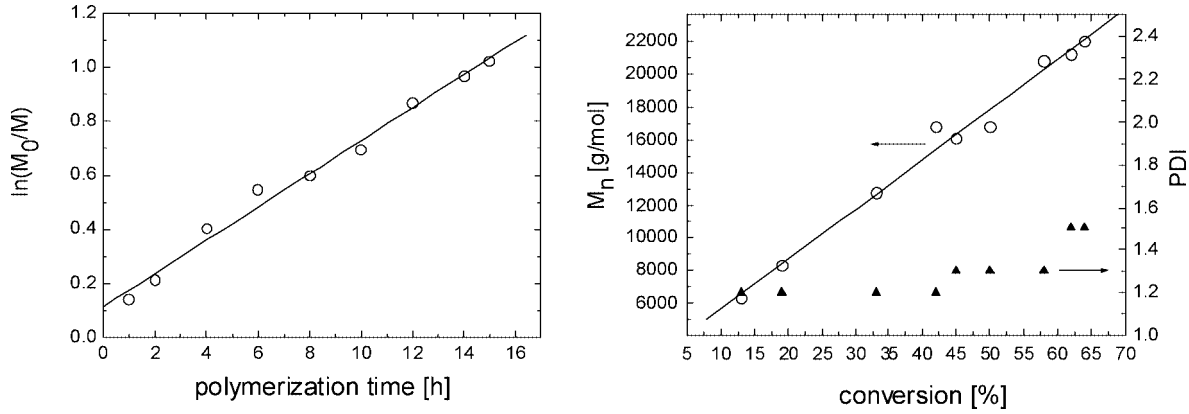


Figure 3. Kinetic plots for the polymerization of **6**: (left) the kinetic plot, (right) $M_{n,experimental}$ (□) and PDI (▲), respectively, vs conversion.

Scheme 3. Synthetic Pathway toward Alkyne-Containing Diblock Copolymers for Polymer Analogous Modification via Click Chemistry and Depiction of Desilylated Target Diblock Copolymers

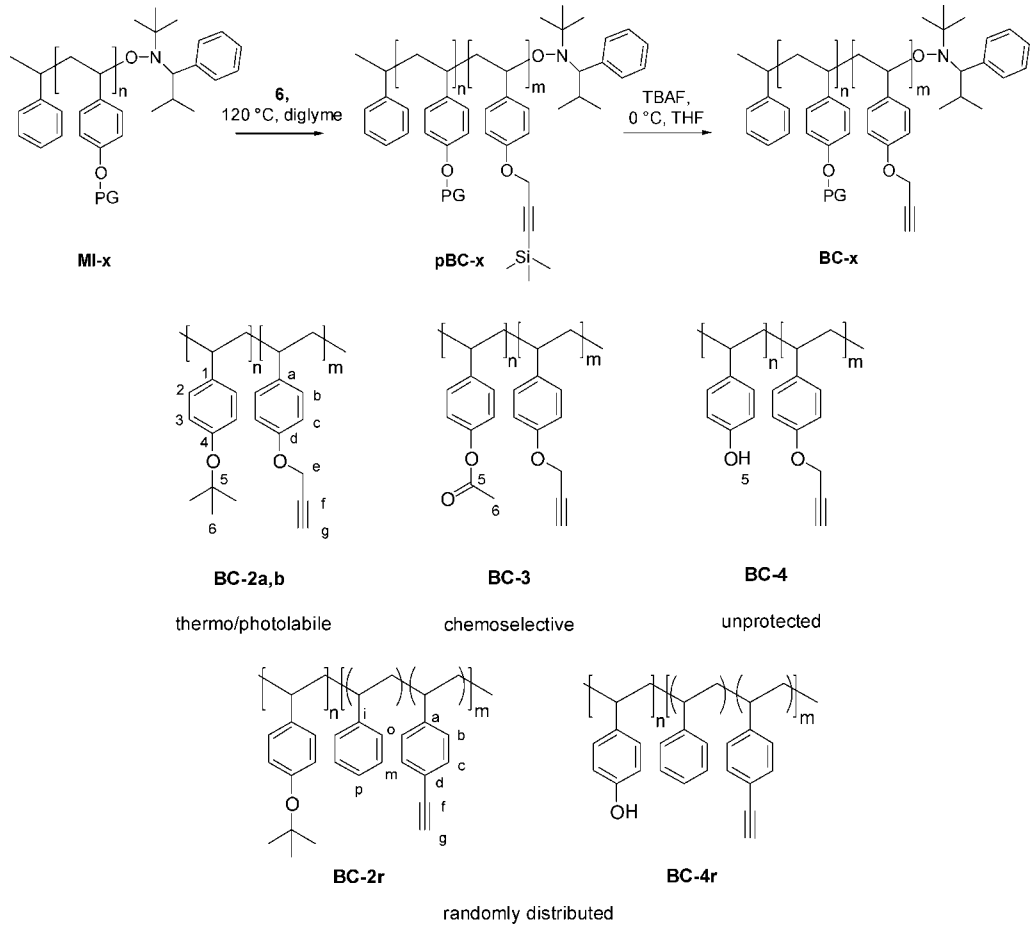


Table 6. Comparison of Calculated and Experimentally (^{1}H NMR) Determined Block Ratios (by Mass) of the Precursor Diblock Copolymers pBC-*x* Synthesized

mass polymer block ratio	pBC-1a	pBC-1r	pBC-2a	pBC-2b	pBC-2r	pBC-3
calculated	1.5:1	1:2.6	1.2:1	5.7:1	2.3:1	2.0:1
NMR	1.6:1	1:3.0	1.4:1	6.4:1	2.5:1	1.8:1

Results and Discussion

Monomer Syntheses. For this work two different alkyne containing monomers based on styrene were used and synthesized, i.e., 4-(trimethylsilylpropargyloxy)styrene (**6**) and 4-(trimethylsilylethynyl)styrene (**7**). Whereas a synthetic procedure for **7** is known in the literature,[23] the method for the preparation of a monomer carrying a more flexible alkyne group needed to be developed. Starting with the commercially available 4-acetoxystyrene (**3**), 4-hydroxystyrene (**4**) was obtained by hydrolysis and subsequently reacted in a straightforward Williamson ether type reaction to yield 4-(propargyloxy)styrene (**5**) (Schemes 1 and 2). Since it is known for alkyne protons to undergo chain transfer in radical polymerizations,[25] the functional group had to be protected. This was best done following a methodology similar as described elsewhere,[26] using chlorotrimethylsilane and DBU in the presence of catalytic amounts of silver chloride. So, **6** could be isolated in acceptable yields of 50−60% overall.

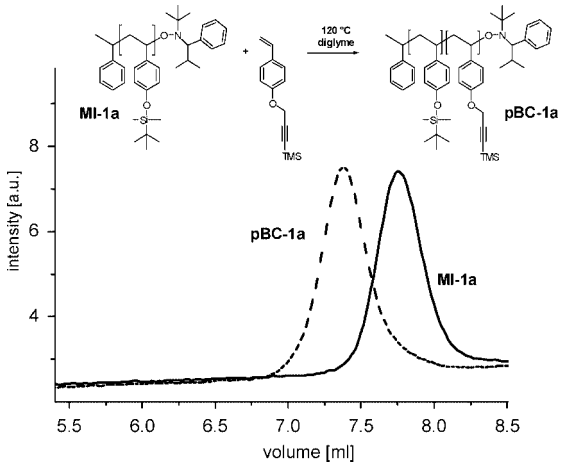


Figure 4. SEC traces of parent macroinitiator **MI-1a** (bold) and the protected diblock copolymer **pBC-1a** (dashed).

The monomers **6** and **7** were selected to develop homo- and diblock copolymer systems with pendent alkyne groups in each repeating unit that can be further used for polymer analogous reactions by click chemistry with regard to attach bulky and sterically more hindered substrates along the backbone. In this context it seems to be interesting whether the alkyne group of **6** that is adjacent to the aromatic ring via a flexible ether bond is more reactive in such polymer analogous modifications as compared to the ethynyl group of **7**. All other monomers used in this study are based on 4-hydroxystyrene, in which the phenolic group is blocked by a labile protective group. The potential use for polymers emanating from labile-protected 4-hydroxystyrene derivatives is the application lithography.[27]

Polymerizations. When thinking about polymer analogous functionalization by click chemistry, Hawker et al.[16,28] were the first who came up with the idea to use **7** in copolymers as well as terpolymers. Hereby, the strength of click chemistry was elegantly demonstrated by a orthogonal one-pot functionalization of terpolymers. However, the alkyne component was incorporated into the polymer with a ratio of 10% only. When considering polymers to be used as scaffolds in macromolecular engineering this might be not enough. Having a polymer fully consisting of pendant alkyne repeating units, real tailoring of material properties can be achieved just by addressing these functionalities in a click reaction, yet starting from the same macromolecule all the time.

Therefore, we started with the synthesis of random copolymers of **7** and styrene by nitroxide mediated radical polymerization using the alkoxyamine initiator **TIPNO-Sty** introduced by the Hawker and Gnanou group.[20] Surprisingly, the PDI of the obtained polymers increased linearly with increasing concentration of **7** in the feed (Figure 1). Finally, for homopolymers of **7** we typically observed polydispersities in the range of 1.9 as well as a poor agreement of the observed molar masses with the calculated number average molar masses (**MI-7b**, Table 5), thus indicating that the controlled nature of the polymerization process was lost.

Adopting a procedure developed for the polymerization of reactive monomers as acrylates, we added free nitroxide **TIPNO** and interestingly found best results when extraordinary high concentrations (more than equimolar with respect to **TIPNO-Sty**) were used (Table 5, **MI-7a**). One possible explanation for this phenomenon is that the recombination reaction in the dormant/active species equilibrium is disturbed by steric hindrance (Figure 1). According to LeChatelier's principle the equilibrium will be shifted more to the left (dormant) side upon addition of free nitroxide, thus lowering the concentration of active chain ends, [P*], and therefore strongly reducing termination reactions ($R_t \sim [P^*]^2$).

If that mismatched equilibrium between active and dormant species was really the case for the poor results regarding the polymerization with **7**, the flexible spacer group linking the alkyne moiety to the aromatic ring in monomer **6** should improve polymerization performance. In fact, the homopolymerization of **6** with the alkoxyamine was found to be drastically improved with good control over the molecular weights and PDIs (Figure 2, Table 5, **MI-6a** and **MI-6b**). In case of 4-(trimethylsilylethynyl)styrene (**7**) only broad molecular weight distributions (Figure 2, dashed line) could be detected for the homopolymers in absence of **TIPNO**, typically bearing a pronounced shoulder toward lower molar masses, whereas for 4-(trimethylsilylpropargyloxy)styrene (**6**) homopolymers symmetric SEC traces were recorded with polydispersities in the range of 1.2−1.3 (Figure 2, bold line).

However, one key factor for the controlled synthesis of poly(4-trimethylsilylpropargyloxy)styrene is the limited stability of the alkyne protecting group. Since the trimethylsilyl group is very unstable toward acidic and basic impurities,[29] we also observed partial deprotection at elevated temperatures used in NMRP conditions. In this case, chain transfer and even crosslinking occurred resulting in insoluble products. This especially happened when acetic anhydride was used as an accelerator.

Considering our experiences with polymers based on protected 4-hydroxystyrene derivatives, where the rate of polymerization as well as uniformity of the final products are enhanced by addition of acetic anhydride it would be advantageous to resort to a more stable protective group as, for instance, the *tert*-butyldimethylsilyl (TBDMS) moiety. Unfortunately, our attempts to synthesize the TBDMS as well as triisopropyl silyl protected analog of **6** were in vain. Therefore, we used monomer **6** without an accelerator in the NMRP process. Kinetic experiments showed that the polymerization of **6** with **TIPNO-Sty** obeys first order kinetic, indicating absence of termination reactions and the M_n vs conversion plot follows linear dependency, thus implying absence of transfer reactions (Figure 3).

Diblock Copolymers. The philosophy behind our work was to develop diblock copolymer systems in such a way that the functional groups of each block can be specifically addressed, both, in solution as well as in thin films.

Starting from one and the same polymer, specific properties could be tuned by directed modification with click chemistry and a library of diblock copolymers could be made by reliable and simple polymer analogous reactions. Another advantage of this modular click approach is the distinct accessibility of basically all kinds of functional groups. With this, by adjusting the functionality of macromolecules as desired, real tailoring of material properties could be achieved and polymers can be created which cannot be synthesized in a direct monomer route.

We started our sequence with the synthesis of the macroinitiators (**MI**) based on 4-hydroxystyrene differently labile protected with *tert*-butyldimethylsilyl- (TBDMS; **MI-1**), *tert*-butyl- (TBU; **MI-2**), and acetyl- (Ac; **MI-3**) groups which were described in a previous communication.[18] With **TIPNO-Sty** as initiator and acetic anhydride as accelerator, the bulk reactions at 120 °C result in final conversions of 70−80%. A good control over the molar mass varying from 7200 g/mol (**MI-1a**) to 43 700 g /mol (**MI-3**) was found and the **MI**s are characterized by low polydispersity indices (Table 1). Detailed NMR analysis showed in all cases that none of the protecting groups was removed upon addition of the accelerator, even in case of the more labile TBDMS group.

This set of macroinitiators **MI-*x*** was subsequently used to initiate the polymerization of **6** as well as a feed of styrene and **7** resulting in the fully protected precursor diblock copolymers

Scheme 4. Synthesis of Diblock Copolymers with Random Distribution of the Alkyne Monomer 7 and Styrene in the Second Block (PG = TBDMS, MI-1b and pBC-1r; PG = TBU, MI-2c and pBC-2r)

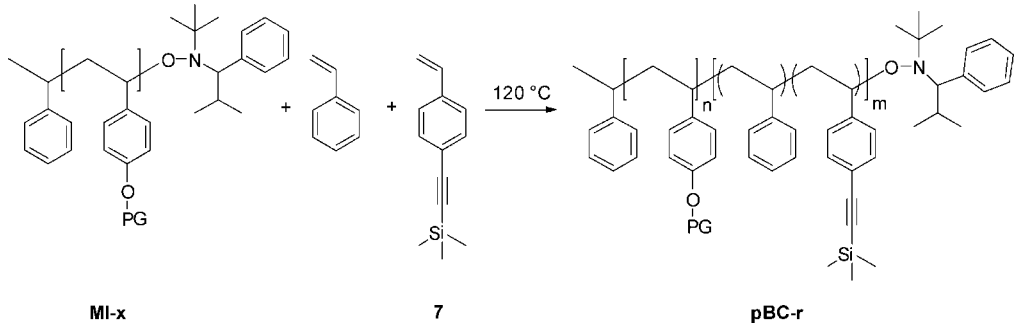


Table 7. Analytical Data of the Target Diblock Copolymers BC-*x* Obtained by Selective Desilylation with (TBA)F

						mass block ratio [B1:B2][a]	
polymer	**pBC-*x***	$M_{n,cal.}$ [g·mol^{-1}]	$M_{n,exp.}$ [g·mol^{-1}]	$M_{w,exp.}$ [g·mol^{-1}]	PDI	calculated	NMR
BC-2a	**pBC-2a**	30800	23400	29500	1.26	1.8:1	1.7:1
BC-2b	**pBC-2b**	56400	52500	63100	1.20	8.3:1	8.5:1
BC-2r	**pBC-2c**	65700	60900	82900	1.36	2.2:1	2.5:1
BC-3	**pBC-3**	27700	21000	29100	1.39	2.8:1	2.5:1
BC-4a	**pBC-1a**	9300				1.2:1	1.1:1
BC-4r	**pBC-1b**	6400				1:5:5	1:5:5

[a] With B1 being the macroinitiator fragment and B2 being the alkyne block.

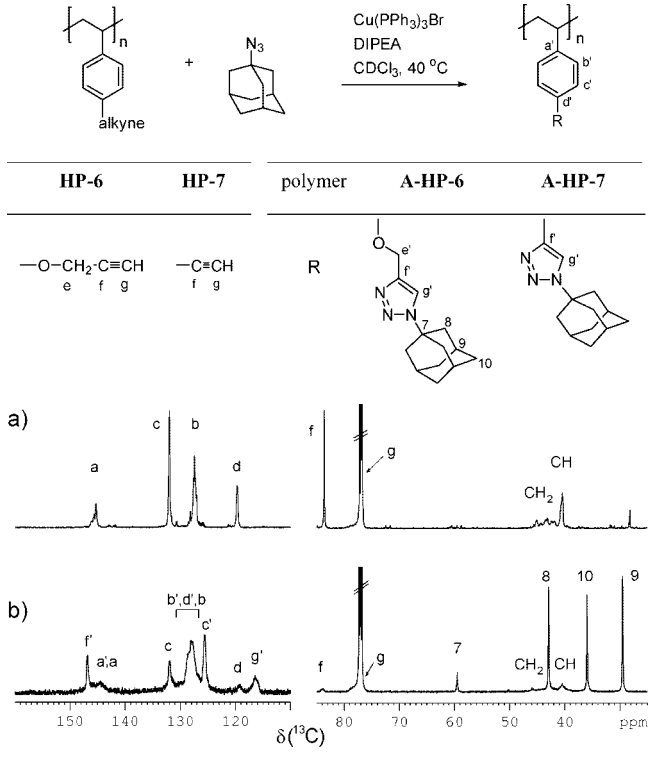


Figure 5. Reaction of the homopolymers **HP-6** and **HP-7** with 1-adamantane azide to form the 1-adamantyl-2,3-triazole substituted polymers **A-HP-6** and **A-HP-7** and ^{13}C NMR spectra of **HP-7** (a) and **A-HP-7** (b) (solvent: $CDCl_3$). Signals of low intensity in the spectrum of **HP-7** are caused by the initiating and terminating group derived from the NMRP initiator.

(**pBC-*x***) (Scheme 3). For this purpose, **6** or a mixture of **7** and styrene, respectively, were sequentially added to the MI and, if needed, a minimum amount of diglyme was used additionally. Again, the polymerization temperatures were kept at 120 °C and the reactions were stopped after 20 h. This time, acetic anhydride could not be added since this would lead to a complete removal of the very labile TMS protective group of **6** and **7** under elevated temperatures. The isolated precursor diblock

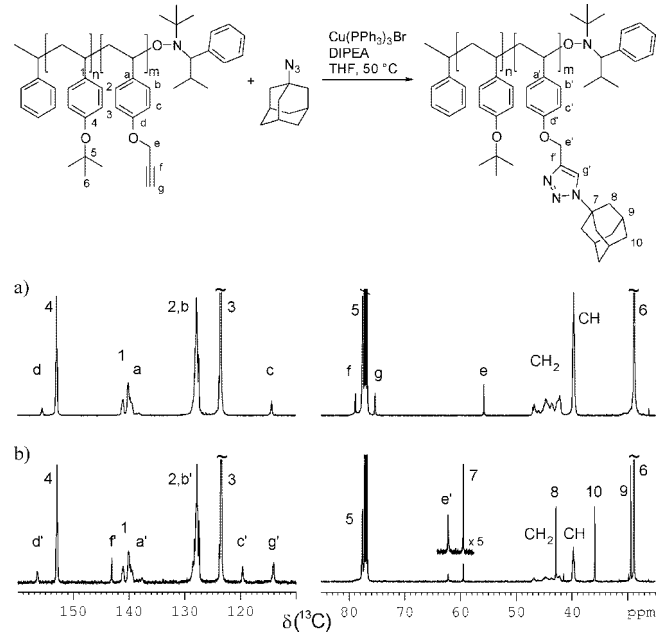


Figure 6. Modification of diblock copolymer **BC-2b** with 1-adamantane azide to form diblock copolymer **A-BC-2b**. Reaction scheme and ^{13}C NMR spectra of **BC-2b** (a) and **A-BC-2b** (b) in $CDCl_3$.

copolymers were entirely protected in both blocks, as indicated by NMR analysis. Block ratios, i.e., M_n(**MI-*x***)/M_n(**Poly-6/7-r-sty**) were experimentally derived from appropriate signal integrals in the ^{1}H NMR spectra (Table 6). They correspond to the molar ratio of the monomers in the copolymer multiplied with the ratio of their molar masses. This ratio was compared with the value obtained from $M_{n,cal}$(**MI-*x***)/$M_{n,cal}$(**Poly-6/7-r-sty**). The molecular weights $M_{n,cal}$(**Poly-6/7-r-sty**) for the second block could be concluded from $M_{n,cal}$(**Poly-6/7-r-sty**) = $\alpha\nu m_{6/(7+sty)}/n_{MI}$ with α is the degree of conversion of monomer **6** and of the mixture of **7** and styrene, respectively.

The efficiency of the reinitiation by the **MI**s can also be evaluated when comparing the SEC traces of the precursor diblock copolymers with its corresponding macroinitiator. As it can be concluded from Figure 4, the reinitiation of **6** with

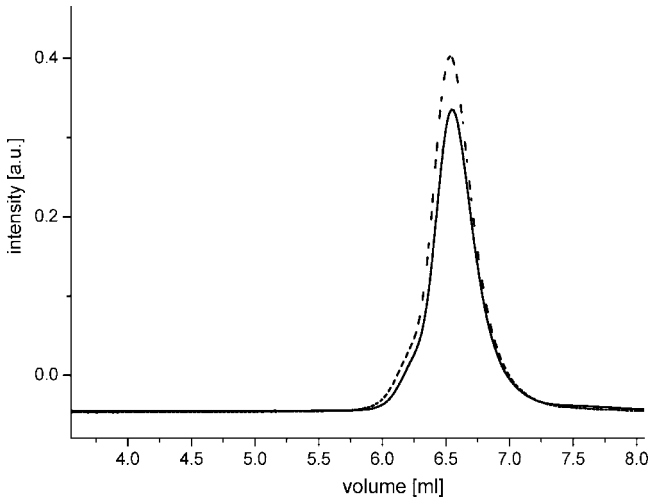


Figure 7. SEC traces of **BC-2** (--) and **A-BC-2b** (—) recorded in chloroform and calibrated versus PS standards.

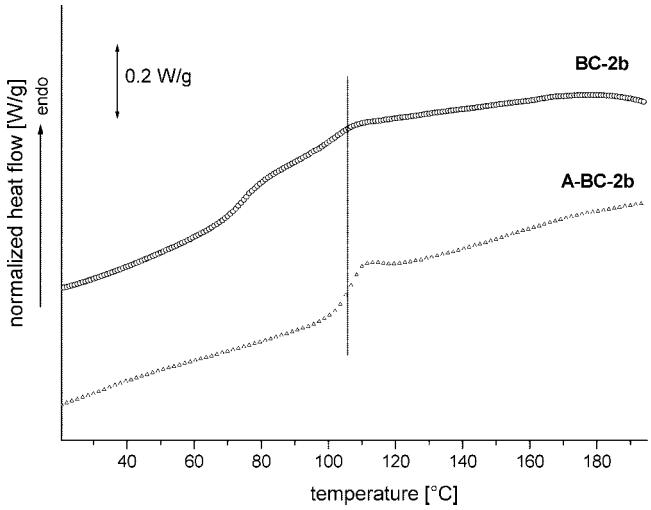


Figure 8. DSC traces of **BC-2b** and its reaction product with 1-adamantane azide, **A-BC-2b**.

MI-1a was complete and products were characterized by a narrow molar mass distribution. Neither a residual **MI** peak nor a shoulder especially toward lower molar masses could be detected in the SEC trace. The same positive findings could be also denoted for all other diblock copolymers when crude material, i.e., prior to the precipitation process, was analyzed.

In the same manner protected diblock copolymers were developed in which the alkyne functionality of the second block is randomly distributed along a styrene backbone (**pBC-1r** and **pBC-2r**). In this case, one has to keep in mind that 4-(trimethylsilylethynyl)styrene (**7**) cannot be incorporated with higher loads than approximately 20% (without using **TIPNO**) in order to preserve the controlled character of the polymerization. Therefore, poly(*tert*-butyloxystyrene) and poly(*tert*-butyldimethylsilyloxystyrene) were used to initiate the copolymerization of styrene and **7** (Scheme 4) with feed compositions of roughly 10:1.

Once more, the reliability of the **MI**-system was proven and macromolecules of a very defined architecture, both, in terms of chemical composition and uniformity were achieved (Table 6).

Click chemistry is the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction between alkynes and azides.[10] The Cu(I) catalysis further provokes an acceleration of an already straightforward cycloaddition, an effect that was first published by Meldal et al.[30] Furthermore, the advantage of the Cu(I) catalysis clearly is the regioselective formation of the 1,4-triazole adduct.[30,31] Since the transition state is assumed to proceed via a copper acetylide species, only terminal alkyne can be efficiently catalyzed.[32] Therefore, the alkyne needs to be deprotected prior to click reaction. Thereby, it is essential to quantitatively and selectively remove all silyl protection groups, while simultaneously leaving the labile protected hydroxystyrene block untouched. The reagents of choice for this purpose are based on fluoride salts and were introduced by Corey et al.[33] Meanwhile, this concept of selective and versatile protection/deprotection has been applied to polymer analogous reactions.[21,34] In fact, referring to tetrabutylammonium fluoride we were able to simultaneously induce the complete removal of all silyl protection groups (i.e., TMS and TBDMS) as well as to preserve all other labile protective groups as confirmed by absence of signals of phenolic moieties in the NMR spectra of **BC-2** and **BC-3**. In case of **pBC-1a,b** also the TMS protecting group of the **MI-1** was removed resulting in poly(hydroxystyrene-*b*-propargyloxystyrene) (**BC-4a**) and poly(hydroxystyrene-*b*-ethynylstyrene-*r*-styrene) (**BC-4r**). If the deprotection was conducted with acids, the TBU and acetoxy groups could not be retained. Therefore, in all experiments the deprotection reactions were carried out in THF at 0 °C with (TBA)F and were shown to have gone to completion after 30 min. Comparing the desilylated target diblock copolymers (**BC-*x***) and its precursor macromolecules the molar mass distributions did not alter. Naturally, however, due to the considerable mass loss, the SEC traces were shifted toward lower molecular weights and mass block ratios changed accordingly; i.e., the contribution of the block originating from the macroinitiator increased since that did not experience degradation upon selective deprotection. Thus, the mass loss obtained in the **BC-1** family led to vast decrease of the B1:B2 ratio (Table 7) with respect to the molar masses. SEC traces of **BC-4a** and **BC-4r** could not be recorded due to adsorption of the material on the column. As the desilylation was shown to be complete in the NMR spectra and since desilylation did not alter the quality of the product for all other diblock copolymers we can assume the same for **BC-4a** and **BC-4r**.

Most of the desilylated block copolymers are phase-separated as indicated by two distinct glass transition temperatures (T_g) in differential scanning calorimetry. In particular for polymers with deblocked hydroxystyrene segments the phase separation seems to be very pronounced due to a high incompatibility of the polar and nonpolar blocks. These diblock copolymers are therefore prime candidates for the preparation of nanostructured surfaces and their phase separation in thin films is currently investigated in our laboratories.

Polymer Analogous Modifications. In the final step, the deprotected target diblock copolymers (**BC-*x***) were reacted with bulky 1-adamantane azide to prove our underlying concept that they are scaffolds for specifically tailoring of macromolecular architecture as well as functionality. Because 1-adamantane azide is a sterically demanding substrate we started with model experiments to evaluate the reactivity of the propargyl and ethynyl group, respectively, in a polymer analogous reaction aiming for an attach-to approach for bulky substituents. In their attentive work Thomsen et al.[35] demonstrated the effective polymer analogous modification of homopolymers as well as random copolymers based on 4-propargyloxystyrene with azido functionalized carboxylic acids. In this case, however, the alkyne polymers originated from polymer analogous reactions of polyhydroxystyrene prepared by free radical polymerization and propargyl bromide, a method which did not allow to prepared defined macromolecular architectures.

Poly(propargyloxystyrene) (**HP-6**) and poly(ethynylstyrene) homopolymer (**HP-7**) with comparable low molecular weights,

i.e., 4400 and 2800 g/mol, respectively, were synthesized and reacted with 1-adamantane azide. Both reactions were conducted under the same conditions at 40 °C with $CDCl_3$ as solvent. For all our experiments we decided to use bromotris(triphenylphosphine)copper as catalyst because of its good solubility in organic solvents. Another advantage is that the active copper(I) species is shielded by the ligands and, thus, oxidative degradation as well as unwanted side reactions are minimized.[36] Typically, in order to enhance the formation of copper acetylide, a bulky tertiary amine base is added; in this work it is diisopropyl ethyl amine (Huenig's base).

The conversion of the alkyne functionalities was monitored by ^{1}H NMR spectroscopy comparing signal intensities characteristic for the nonreacted and reacted functionalities. In case of **HP-6** the oxymethylene protons bonded to the ethynyl ($\delta(H_e)$ = 4.63 ppm) and triazole group ($\delta(H_e')$ = 5.1 ppm) were followed whereas the decrease of the ethynyl proton signal ($\delta(H_g)$ = 3.07 ppm) was monitored for **HP-7**. Full conversion was achieved for **HP-6** after 300 h at 40 °C and the reaction obeys a first order kinetics. In contrast, polymer **HP-7** did not react quantitatively with adamantane azide and only a conversion of 70% could be achieved within the same period of time. The higher reactivity of the propargyl group is obviously because of the additional oxymethylene spacer between phenyl ring and ethynyl group reducing the steric hindrance between the reactive sites of the phenyl groups along the polymer backbone. That the formation of 1-adamantyl-2,3-triazole substituents hinders the overall backbone mobility can be concluded both from increase of the line widths in the NMR spectra which is especially pronounced for **A-HP-7** despite the lower conversion (Figure 5) and from DSC analysis.

DSC analysis of the samples indicated that the chain flexibility drastically decreased. This can be concluded from a remarkable increase of the T_g from 54 °C in case of the starting polymer **HP-6** up to 168 °C for the corresponding adamantane "clicked" polymer **A-HP-6**. In absence of the oxymethylene spacer, i.e. for **A-HP-7**, no T_g could be observed up to 220 °C when decomposition started. These findings are in accordance with the transformation of a random polymer coil into a more stretched structure which is aimed at the introduction of the bulky substituents.

Turning from the polymer analogous modification of model homopolymers to the modification of diblock copolymers, the poly(propargyloxystyrene) containing systems are obviously the most promising candidates to realize a complete conversion of alkyne to triazole groups by azide addition. For reasons of comparison with the homopolymer, again the bulky and sterically demanding 1-adamantane azide was reacted with poly(*tert*.-butyloxystyrene)-*block*-poly(propargyloxystyrene) (**BC-2b)** under conditions similar as described above (Figure 6, top). At slightly higher temperature compared to the model study (50 °C vs 40 °C) it could be proved by ^{1}H NMR spectroscopy that the propargyl groups were completely converted within 48 h finally resulting in the diblock copolymer **A-BC-2b**.

By comparison of the ^{13}C NMR spectra of **BC-2b** (Figure 6a) and **A-BC-2b** (Figure 6b) the disappearance of the propargyl carbon signals C_e−C_g and the occurrence of both the methyleneoxy triazole signals C_e'−C_g' and the adamantly carbon signals C_7−C_{10} confirm the new structure. There is no indication of a notable side reaction. The smooth transformation of the alkyne groups containing polymer fragment consequently resulted in the formation of a new, highly defined macromolecule.

The comparison of SEC traces recorded in chloroform (Figure 7) shows molar mass distributions that are nearly identical for both, the starting block copolymer and its reaction product. A more or less pronounced shoulder toward lower molar masses indicating imperfect decoration of the polymer backbone was not observed in accordance with the NMR results showing no structural defects. The SEC traces are symmetrical, exhibiting narrow molecular weight distributions with a polydispersity index of 1.20. Despite the increasing molar mass of **A-BC-2b** compared with the educt **BC-2b** the elution volume remained constant and the molar mass obtained (M_n = 54 100 g/mol) with PS-calibration is too low compared to the theoretically calculated value (M_n = 63 300 g/mol). This shows the limitations of the polystyrene calibration for the modified block copolymer products.

The decoration of the polymer backbone with adamantane units led to drastically altered calorimetric properties of the block copolymer (Figure 8). In **BC-2b** two single T_gs could be extracted from the DSC curves at 74 and 102 °C, attributed to the propargylstyrene and TBU-oxystyrene block, respectively. After complete "clicking" of 1-adamatane azide the lower T_g vanished entirely and only the glass transition for the TBU-block at 102 °C appeared. We can compare these findings with the situation found for **HP-6** and **A-HP-6** where the attachment of adamantane units resulted in an increase of the T_g from 54 to 168 °C or even in a complete loss of a T_g in the studied temperature region up to 220 °C as found for **A-HP-7**. The steric demand imposed by the bulky adamantane side chains might also induce a bracing of the former propargyl block leading to a high rigidity, thus increase of the glass transition to a higher and not detectable value.

The effects observed after introduction of the bulky adamantly moiety point to more general conclusions. By modification of polymers with appropriate azides via click chemistry the secondary structure of macromolecules can be triggered as desired. This would, for instance, give rise to the idea that dendronized diblock copolymers of a rod−coil-type structure can be generated by a versatile attach-to "click" approach of the corresponding dendritic azides along alkyne polymers. This issue is currently under investigation in our group, and first experiments gave convincing results.

Conclusion

A set of different alkyne containing diblock copolymers based on 4-hydroxystyrene was synthesized by nitroxide mediated radical polymerization (NMRP) using the macroinitiator method, all with excellent control over the molecular composition and narrow molar mass distribution. The materials consist of labile protected 4-hydroxystyrene motifs in one block and bear alkyne functionalities in each repeating unit of the second block, thus making the materials candidates for block copolymer lithography and polymer analogous modification reactions by a very efficient cycloaddition reaction (click chemistry). The use of 4-(trimethylsilylpropargyloxy)styrene as monomer proved highly advantageous compared to 4-(trimethylsilylethynyl)styrene, first because high control was kept in the NMRP process and second, because higher accessibility was obtained in the postmodification reaction.

The products were characterized with various analytical means (NMR, SEC, DSC) which allowed to prove the chemical composition and the high control achieved in NMRP. The diblock copolymers showed pronounced phase separation as indicated by calorimetric measurements. The Cu(I)-catalyzed cycloaddition reaction of the pending propargyloxy groups with even bulky azides—as model adamantine azide was used—was successfully employed for the modular quantitative postfunctionalization of the diblock copolymers. In the alkyne homopolymers as well as in the block copolymers, a significant increase in T_g was observed after the modification with pendant adamantane units allowing the conclusion that the coil structure of the polymer chain has been transferred into a more rigid form.

Once more, the combination of controlled polymerization techniques and click chemistry demonstrated to be a powerful tool for the manipulation and functionalization of macromolecules.

The presented alkyne containing block copolymers can be considered as macromolecular scaffolds and a further impact in the emerging field of nanoscience can be expected. "Clicking" functionalization onto nanostructured films of such kind of diblock copolymers with high spatial resolution is certainly of great scientific interest. This issue is currently being investigated in our institute.

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Supporting Information Available: Text giving a detailed structure elucidation by NMR as well as IR spectroscopy for all macroinitiators and diblock copolymers. This information is available free of charge via the Internet at http://pubs.acs.org.

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