New Photolabile Functional Polymers for Patterning onto Gold Obtained by Click Chemistry

Barbara Sieczkowska, Marta Millaruelo, Martin Messerschmidt, and Brigitte Voit*

Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Received October 19, 2006; Revised Manuscript Received January 17, 2007

ABSTRACT: Nitroxide-mediated radical polymerization (NMRP) was used for the synthesis of the random copolymer poly[styrene-*r*-(4-propargyloxystyrene)] with a narrow molecular weight distribution (PDI ∼ 1.2). The material was postfunctionalized by polymer analogous reactions and via Cu(I)-catalyzed 1,3-dipolar cycloadditions ("click chemistry approach") to provide a family of photopatternable functional polymers for nanotechnology applications. For this, a series of azides were designed in order to incorporate subunits with specific properties into the materials. Photopatterning was made possible by the introduction of units with a photoremovable amino protecting group (PRG) (nitroveratryloxycarbonyl, NVOC) which may lead to the release of amino functions after selective UV/laser irradiation. Covalent attachment of the functional polymers onto gold was promoted by sulfide-containing anchoring units again introduced as pending groups onto the polymer backbone via the 1,3-dipolar cycloaddition reaction. The modified materials were obtained in almost quantitative yields under mild conditions according to IR and NMR studies. Thermal characterization was accomplished by DSC and TGA. Click chemistry is once more proven to be a useful tool for material science, in this particular case for the preparation of functional polymers for photopatterning with modulated properties.

Introduction

During the past 10 years there is a rising demand to obtain functional polymers with well-defined and controllable structures, especially in nanoscience and nanotechnology, where the structure of the materials assumes a crucial role because of the small size scales involved.[1]

Nowadays, there is a wide range of techniques grouped under the name controlled radical polymerization (CRP) which constitute an exciting research field and attract substantial interest, from both an industrial and academic point of view. They are adequate for the preparation of polymers with assorted macromolecular architectures, controlled molecular weight and polydispersity index, and specific end-functional groups, allowing the targeting of materials with tunable properties and hence specific applications.[2−6] Among them, NMRP is an important synthetic tool whose development has been extremely rapid with exciting possibilities for the future.[4]

Functional polymers embrace conductive polymers, liquid crystals, photoactive polymers, polymers for biomedical applications, and materials to accomplish patterning on a variety of substrates, and using them fabrication of devices with specific functions has been accomplished.[7−10] These materials can promote the patterning of structures with high fidelity and structuring in the nanoscale. Besides, the multifunctionality enables interesting applications as can be specific molecular recognition functions, microfluidic devices, or sensors.[11,12]

Click reactions encompass a set of techniques which allow the functionalization or construction of macromolecules of very diverse nature[13−19] in nearly quantitative yields. They are well-known for the broad tolerance toward functional groups low susceptibility to side reactions allowing mild reaction conditions and easy workup of final products.[20,21] One of the most efficient is the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between terminal acetylenes and azides to yield a stable 1,4-disubstituted 1,2,3-triazole ring.[22]

* To whom correspondence should be addressed: Fax +49 351 4658565; e-mail voit@ipfdd.de.

Click chemistry allows the preparation of multifunctional materials in combination with other synthetic transformations in quantitative yields, allowing furthermore absolute fidelity. Development of cascade and simultaneous functionalization approaches for the preparation of multifunctional materials has been explored by Malkoch et al.,[23] in which a combination of previously functionalized and nonfunctionalized monomers was used for the preparation of materials ready for further modifications using the mentioned strategies.

Here we present an approach combining the advantages of controlled radical polymerization (NMRP) and click chemistry for the synthesis of side-functionalized copolymers. We have chosen as starting material the random copolymer poly[styrene-*r*-(4-acetoxystyrene)] obtained from styrene and 4-acetoxystyrene, monomers which can be easily polymerized by NMRP and with the advantage that they can be commercially purchased. The subsequent polymer is transformed by further cascade reactions into an adequate precursor polymer for the performance of click reactions, as has resulted to be poly[styrene-*r*-(4-propargyloxystyrene)]. Later on a family of azides has been selected to modulate the properties of the polymers using the "click chemistry approach". The incorporation of photolabile amino protecting groups in the materials may enable the release of functional groups by means of UV/laser irradiation. On the other hand, the incorporation of sulfide derivatives as anchoring groups allows the covalent attachment of the materials onto gold substrates. This feature will allow further reactivity or modifications of the functional groups of thin polymer films in liquid media, for example, for the formation of supramolecular interactions or the attachment of nanoelements. Previous research has been done in our laboratories in which random co- and terpolymers obtained by free radical polymerization were used for similar objectives.[24−28] The system presented here allows the preparation of multiple modified materials in a single step using a common precursor. Besides, control of the molecular weight of the materials is achieved.

10.1021/ma062410z CCC: $37.00
Published on Web 03/01/2007

Thus, in this work we show a novel extension of click chemistry for the preparation of functional and structurally near-perfect polymers consisting of simple units, with great potential for surface applications in lithographic functional patterning and nanotechnology. Synthesis and characterization of these materials are exposed.

Experimental Part

Materials. DL-α-Lipoic acid (98%, Fluka), 6-chloro-1-hexanol (99%, Fluka), sodium azide (99,5%, Fluka), 18-crown-6 (99%, Aldrich), 4-azidoaniline hydrochloride (97%, Aldrich), dicyclohexylcarbodiimide (DCC) (98%, Fluka), 4-(dimethylamino)pyridine (DMAP) (99%, Fluka), 6-nitroveratryl chloroformate (NVOC) (97%, Fluka), L-methionine (99.5%, Fluka), azidomethylphenyl sulfide (95%, Aldrich), azidophenyl isothiocyanate (97%, Aldrich), 11-azido-3,6,9-trioxamindecene-1-amine (90%, Fluka), acetoxystyrene (96%, Aldrich), hydrazine monohydrate (99%, Fluka), and propargyl bromide (80% (w/w) toluene solution, Across) were purchased and directly used without further purification. Styrene (99%, Fluka) was destabilized by elution over a basic Al_2O_3 column and subsequent distillation under pressure. Acetic anhydride (99%, Riedel-de Haen), diethyl ether, dioxane, dichloromethane, DMF, pyridine, and *N*,*N*-diisopropylethylamine (DIPEA) were purchased from Fluka and dried prior to use over molecular sieves. Initiator 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TPPA) used for the synthesis of the materials through NMRP was obtained following the procedures described in the literature.[29,30]

Instruments. ^{1}H NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer (Bruker, Billerica, MA) at 500.13 MHz, and ^{13}C NMR spectra were recorded at 125.74 MHz. All of them were measured in $CDCl_3$ or DMSO-d_6, and the solvent was used as a internal standard. FTIR were recorded in a transmission mode using a Bruker IFS 66 v/s spectrometer (Bruker, Billerica, MA) with a resolution of 4 cm^{-1} (32 scans). The relative molecular weights of the polymers were determined by gel permeation chromatography (GPC) in chloroform using a modular Knauer system with RI detector and LIChrogel PS40 column and applying linear calibration with polystyrene. EA analysis were carried out with a Elementar Analyses System GmbH. Microcalorimetric studies were carried out using a DSC Q1000 (TA Instruments) with a heating rate of 20 K/min under a N_2 atmosphere (−60 °C−Ti). Thermogravimetric analysis were performed using a TGA Q500 (TA Instruments) at a heating rate of 10 K/min under a N_2 atmosphere (30−800 °C).

Synthesis of 5-[1,2]Dithiolan-3-yl-pentanoic Acid 6-Azidohexyl Ester (a). To a solution of lipoic acid (1.03 g, 5 mmol) dissolved in anhydrous diethyl ether (10 mL), DMAP (0.12 g, 1 mmol) and 6-chloro-1-hexanol (0.94 g, 6.6 mmol) were added, and this mixture was cooled between −10 and −5 °C. Finally, DCC (1.13 g, 5.5 mmol), previously cooled down to this temperature, was added. The reaction mixture was stirred under these conditions for 1.5 h, after that at 5 °C for 1.5 h, and finally for 4 h at room temperature. The white powder which appeared in the solution was filtered, and the filtrate was diluted with diethyl ether (3 × 50 mL), washed with water (2 × 50 mL), and finally dried over Na_2SO_4. After filtration the solvent was removed under reduced pressure. The azide was obtained as a yellow viscous liquid. Yield: 63%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.06 (t, 2H); 3.54 (m, 1H); 3.24 (t, 2H); 3.15 (m, 1H); 3.09 (m, 1H); 2.43 (m, 1H); 2.29 (t, 2H); 1.88 (m, 2H); 1.66−1.43 (m, 10H); 1.37 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 173.38, 64.08, 56.24, 51.23, 40.11, 38.37, 34.82, 34.49, 33.98, 28.64, 28.42, 26.26, 25.44, 24.60. IR (KBr): (ν, cm^{-1}) = 2931−2858 ($\nu_{s,as}$ CH_2), 2091 (ν N_3), 1729 (ν COO), 1456 (δ CH_2), 1239 (ν CH Ar), 1169 (ν C−O). Anal. Calcd for $C_{14}H_{25}N_3O_2S_2$: C, 50.72%; H, 7.60%; N, 12.68%; S, 19.35%. Found: C, 49.94%; H, 6.45%; N, 12.32%; S, 19.18%.

Synthesis of 6-Azidohexylcarbonic Acid 4,5-Dimethoxy-2-nitrobenzyl Ester (b). To a mixture of 1 mmol of 6-azido-1-hexanol (0.14 g), 3 mmol (0.24 g) of pyridine, and 10 mL of CH_2Cl_2 at −5 °C a solution of 3 mmol (0.83 g) of NVOC-Cl dissolved in 10 mL of CH_2Cl_2 was added slowly. The reaction was stirred for 0.5 h at −5 °C under a nitrogen atmosphere and then overnight at room temperature. This mixture was then poured into ice water, and the aqueous phase was extracted with CH_2Cl_2. Afterward, the organic extracts were collected and washed with a HCl 5% (w/w) aqueous solution and finally dried over Na_2SO_4. After filtration the solvent was removed under reduced pressure, and the product was purified by chromatographic column using as eluent a mixture of ethyl acetate/hexane 2:3 (v/v). The product was obtained as a yellow oil. Yield: 51%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.71 (s, 1H); 7.67 (s, 1H); 7.09 (s, 1H); 7.05 (s, 1H); 5.56 (s, 2H); 5.00 (s, 2H); 4.18 (t, 2H); 3.99 (d, 6H); 3.95 (s, 6H); 3.26 (t, 2H); 1.71 (m, 2H); 1.60 (m, 2H); 1.41 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 154.65, 153.56, 148.23, 139.62, 126.66, 109.88, 108.11, 66.04, 56.32, 51.16, 28.56, 28.39, 26.18, 25.15. IR (KBr): ν (cm^{-1}) = 2943 ($\nu_{s,as}$ CH_2), 2861 (ν OCH_3), 2112 (ν N_3), 1740 (ν CO), 1524 (ν_{as} NO), 1433 (δ CH_2), 1328 (ν_s NO), 1266 (ν CO), 1062 (ν CO), 796−790 (δ CH Ar). Anal. Calcd for $C_{16}H_{22}N_4O_7$: C, 50.26%; H, 5.80%; N, 14.65%. Found: C, 48.96%; H, 5.12%; N, 11.61%.

Synthesis of 2-(4,5-Dimethoxy-2-nitro-benzyloxycarbonylamino)-4-methylsulfanylbutyric Acid (c). L-Methionine (0.149 g, 1 mmol) and $NaHCO_3$ (0.21 g, 2.5 mmol) were dissolved in 20 mL of water. Then NVOC-Cl (0.304 g, 1.1 mmol) was dissolved in 28 mL of dioxane and added to the aqueous solution under stirring. After 18 h, the solution was concentrated to approximately one-third of the volume under vacuum. The mixture was acidified with acetic acid, and the precipitate obtained was filtered, washed several times with diluted acetic acid, and then dried under high vacuum. The product was isolated via chromatographic column using as eluent a mixture of ethyl acetate/hexane 2:3 (v/v). The product was obtained as a light yellow solid. Yield: 74%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 12.69 (br, 1H); 7.84 (d, 1H); 7.70 (s, 1H); 7.18 (s, 1H); 5.39 (q, 2H); 4.11 (m, 1H); 3.92 (s, 1H); 3.87 (s, 1H); 2.54 (m, 2H); 2.03 (s, 3H); 1.99 (m, 1H); 1.90. ^{13}C NMR (500 MHz, DMSO): δ (ppm) = 173.70, 155.93, 153.65, 147.87, 139.20, 128.34, 110.19, 108.31, 62.55, 56.34, 56.25, 52.96, 30.59, 29.94, 14.64. IR (KBr): ν (cm^{-1}) = 3553 (ν OH), 3308 (ν NH), 3100−3019 (ν CH Ar), 2920 ($\nu_{s,as}$ CH_2, CH_3), 2851 (ν OCH_3), 1682 (ν COO, COONH), 1581 (amide II), 1517 (ν_{as} NO), 1440 (δ CH_2), 1423 (δ CH), 1381 (δ_s CH_3), 1324 (ν_s NO), 1270 (ν CO), 1064 (ν CO), 795−784 (δ CH Ar). Anal. Calcd for $C_{15}H_{20}O_8N_2S$: C, 46.3%; H, 5.15%; N, 7.22%; S, 8.25%. Found: C, 45.90%; H, 4.77%; N, 7.07%; S, 8.34%.

Synthesis of 2-(4,5-Dimethoxy-2-nitrobenzyloxycarbonylamino)-4-methylsulfanylbutyric Acid 6-Azidohexyl Ester (c). NVOC MeS (0.388 g, 1 mmol) and 1,1′-carbonyldiimidazole (CDI) (0.162 g, 1 mol) were dissolved in 50 mL of dry THF and stirred at ambient temperature overnight. Then 6-azido-1-hexanol (0.86 g, 6 mmol) was added to the stirred solution. The solution was stirred at 67 °C for 24 h under reflux, and finally ethanol (40 mL) was added dropwise to the mixture. The reaction mixture was stirred under these conditions for 6 h. The solvent was removed under reduced pressure, and the product was purified by chromatographic column using as eluent a mixture of ethyl acetate/hexane 7:3 (v/v). The product was obtained as a yellow solid. Yield: 48%. ^{1}H NMR (500 MHz, DSO): δ (ppm) = 7.97 (d, 1H); 7.71 (s, 1H); 7.18 (s, 1H); 5.38 (q, 2H); 4.20 (m, 1H); 4.05 (m, 2H); 3.92 (s, 1H); 3.87 (s, 1H); 3.29 (t, 2H); 2.53 (m, 2H); 2.03 (s, 3H); 1.95 (m, 1H); 1.92 (m, 1H); 1.54 (m, 2H); 1.49 (m, 2H); 1.30 (m, 4H). ^{13}C NMR (500 MHz, DMSO): δ (ppm) = 172.21, 155.88, 153.57, 147.89, 139.35, 127.96, 110.49, 108.33, 64.60, 62.67, 56.34, 56.24, 52.96, 50.69, 30.78, 30.42, 29.73, 28.22, 28.04, 25.80, 14.58. IR (KBr): ν (cm^{-1}) = 3308 (ν NH), 3101 (ν CH Ar), 2936 ($\nu_{s,as}$ CH_2, CH_3), 2088 (ν N_3), 1740 (ν CO), 1693 (ν COO, COONH), 1578 (amide II), 1522 (ν_{as} NO), 1437 (δ CH_2), 1423 (δ CH), 1381 (δ_s CH_3), 1320 (ν_s NO), 1275 (ν CO), 1066 (ν CO), 796 (δ CH Ar). Anal. Calcd for $C_{21}H_{31}N_5O_8S$: C, 49.11%; H, 6.08%; N, 13.64%; S, 6.24%. Found: C, 49.26%; H, 5.08%; N, 13.11%; S, 6.07%.

Synthesis of (2-{2-[2-(2-Azidoethoxy)ethoxy]ethoxy}ethyl)-carbamic Acid 4,5-Dimethoxy-2-nitrobenzyl Ester (d). 11-Azido-

3.6.9-trioxane undecane-1-amine (0.22 g, 1 mmol) and $NaHCO_3$ (0.21 g, 2.5 mmol) were dissolved in water (20 mL), and a solution of NVOC-Cl (0.83 g, 3 mmol) in dioxane (28 mL) was added. The reaction mixture was kept under stirring for 18 h and afterward diluted with ethyl acetate. The aqueous layer was extracted (3 × 50 mL) with ethyl acetate, washed with water (2 × 50 mL), and finally dried over Na_2SO_4. After filtration the solvent was removed under reduced pressure, and the product was isolated via column chromatography using as eluent a mixture of ethyl acetate/hexane 7:3 (v/v). The product was obtained as light yellow solid. Yield: 47%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.69 (s, 1H), 7.02 (s, 1H), 5.50 (br, 3H), 3.97−3.94 (s, 6H), 3.66 (br, 4H), 3.64 (br, 2H), 3.57 (t, 2H), 3.41 (q, 2H), 3.36 (t, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 156.0, 153.50, 148.20, 139.97, 125.48, 110.63, 108.20, 70.50, 70.22, 69.90, 63.55, 56.45, 56.39, 40.98. IR (KBr): ν (cm^{-1}) = 3350 (ν NH), 3101 (ν CH Ar), 2922 ($\nu_{s,as}$ CH_2, CH_3), 2062 (ν N_3), 1694 (ν CO), 1609 (νC=C Ar), 1511 (ν_{as} NO), 1452 (δ CH_2), 1327 (ν_s NO), 1270 (ν CO), 1062 (ν CO). Anal. Calcd for $C_{19}H_{30}N_8O_{10}$: C, 43.02%; H, 5.70%; N, 21.12%. Found: C, 46.92%; H, 5.96%; N, 15.17%.

Synthesis of (4-Azidophenyl)carbamic Acid 4,5-Dimethoxy-2-nitrobenzyl Ester (e). 4-Azidoaniline hydrochloride (0.171 g, 1 mmol) and $NaHCO_3$ (0.21 g, 2.5 mmol) were dissolved in water (20 mL), and under stirring a solution of NVOC-Cl (0.304 g, 1.1 mmol) in dioxane (28 mL) was added. The reaction mixture was kept under stirring for 24 h. The emerging precipitate was separated and afterward was diluted with ethyl acetate. The aqueous layer was extracted (3 × 50 mL) with ethyl acetate, washed at first with 0.1 N HCl (50 mL) and then with water (50 mL) and brine (50 mL). Finally, the solution was dried over Na_2SO_4. After filtration the solvent was removed under reduced pressure, and the product was isolated via column chromatography using as eluent a mixture of ethyl acetate/hexane 1:1 (v/v). The product was obtained as a light yellow solid. Yield: 58%. ^{1}H NMR (DMSO): 9.91 (s, 1H), 7.72 (s, 1H), 7.51 (d, 2H), 7.28 (s, 1H), 7.07 (d, 2H), 5.45 (s, 2H), 3.91 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (DMSO): 153.30, 153.04, 148.08, 139.82, 136.22, 133.45, 126.70, 119.87 (br) 114.57, 111.70, 108.32, 62.98, 56.37, 56.17. IR (KBr): ν (cm^{-1}) = 3347 (ν NH), 3071−3015 (ν CH Ar), 2921 ($\nu_{s,as}$ CH_2, CH_3), 1739 (ν COO, NHCOO), 1608 (ν C=C Ar), 1523 ($\nu_{s,as}$ −N=O), 1510 (ν C=C Ar), 1458 (δ CH_2), 1335 (ν_s NO), 1278 (ν CO), 757−698 (δ CH Ar). Anal. Calcd for $C_{16}H_{15}N_5O_6$: C, 51.48%; H, 4.05%; N, 18.76%. Found: C, 49.79%; H, 3.62%; N, 11.13%.

Synthesis of Poly(styrene-*r*-4-acetoxystyrene) (1). Styrene (18.96 g, 0.18 mol), acetoxystyrene (3.28 g, 0.02 mol), nitroxide initiator (TPPA) (0.46 g, 7.4×10^{-4} mol), and acetic anhydride (0.15 g, 1.48×10^{-3} mol) were introduced in a 250 mL flask. The mixture was degassed with four freeze/thaw cycles, and then it was kept under a nitrogen atmosphere. Afterward, it was immersed in an oil bath preheated at 120 °C for 16 h, and at the end of the reaction it was cooled to room temperature. The reaction bulk was dissolved in CH_2Cl_2, precipitated in ethanol, and reprecipitated two times also in ethanol for purification. The material obtained was dried at 50 °C under vacuum overnight and was obtained as a white solid. Yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.07 (br, 2H); 6.57 (br, 3H); 2.26 (br, 3H); 1.83 (br, CH); 1.42 (br, CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 169.20, 148.63, 145.31, 142.89, 127.96, 125.65, 120.86, 43.89, 40.41, 30.85, 21.16. IR (KBr): ν (cm^{-1}) = 3060−3026 (ν CH Ar), 2920 ($\nu_{s,as}$ CH_2), 1761 (ν COO), 1602 (ν C=C Ar), 1493 (ν C=C Ar), 1451 (δ CH_2), 1366 (ν $OCOCH_3$), 1197 (ν CO), 756 (δ CH Ar). Anal. Calcd for $[C_{8.22}H_{7.33}O_{0.22}]$: C, 90.09%; H, 6.69%. Found: C, 89.03%; H, 7.65%.

Synthesis of Poly[styrene-*r*-(4-hydroxystyrene)] (2). Poly(styrene-*r*-4-acetoxystyrene) **(1)** (3.47 g, 0.02 mol) was dissolved in dioxane (200 mL). The solution was stirred for 0.5 h at room temperature, and hydrazine monohydrate (6.43 g, 0.13 mol) was added to the solution. The reaction mixture was stirred for 12 h, then concentrated under vacuum, and precipitated in a mixture of water/methanol (1:9, v/v). The product was obtained as a white solid. The material obtained was dried at 50 °C under vacuum overnight and was obtained as a white solid. Yield: 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.07 (br, 2H); 6.57 (br, 3H); 5.30 (br, 1H); 1.83 (br, CH); 1.43 (br, CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 153.24, 145.3, 137.50, 129,5−127.90 (3C), 125.6, 114.92, 43.9, 40.37. IR (KBr): ν (cm^{-1}) = 3532 (ν OH), 3060−3026 (ν CH Ar), 2920 ($\nu_{s,as}$ CH_2), 1602 (ν C=C Ar), 1493 (ν C=C Ar), 1451 (δ CH_2), 756 (δ CH Ar). Anal. Calcd for $[C_{8.00}H_{7.11}O_{0.11}]$: C, 91.54%; H, 6.78%. Found: C, 89.17%; H, 8.1%.

Synthesis of Poly[styrene-*r*-(4-propargyloxystyrene)] (3). Poly(styrene-*r*-4-hydroxystyrene) **(2)** (10 g, 9.46×10^{-3} mol), K_2CO_3 (3.92 g, 0.03 mol), and 18-crown-6 (0.054 g, 2.05×10^{-4} mol) were placed in a 150 mL flask and dissolved in DMF (40 mL). The mixture was degassed several times and kept under a nitrogen atmosphere. While stirring for 15 min at room temperature, propargyl bromide (1.4 g, 0.02 mol) was added to the solution under a nitrogen atmosphere. The mixture was stirred at 50 °C for 12 h and cooled to room temperature. The remaining K_2CO_3 left in the reaction medium was removed by filtration. The polymer solution was concentrated under reduced pressure and afterward dissolved in CH_2Cl_2 and precipitated in methanol. The material obtained was dried at 50 °C under vacuum overnight and was obtained as a white solid. Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.08 (br, 2H); 6.57 (br, 3H); 4.59 (br, 2H); 2.45 (br, 1H); 1.82 (br, CH); 1.42 (br, CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 155.6, 145.3, 138.3, 129,5−127.8 (3C), 125.6, 114.42, 78.95, 75.25, 55.90, 43.9, 40.39. IR (KBr): ν (cm^{-1}) = 3288 (ν C≡CH), 3059−3025 (ν CH Ar), 2921 ($\nu_{s,as}$ CH_2), 2120 (ν C≡CH), 1659 (ν Ar−CO), 1601 (ν C=C Ar), 1493 (ν C=C Ar), 1452 (δ CH_2), 1217 (ν COC), 1029, 757−697 (δ CH Ar). Anal. Calcd for $[C_{8.33}H_{7.33}O_{0.11}]$: C, 91.66%; H, 6.72%. Found: C, 89.10%; H, 7.22%.

General Procedure for the Modification of Polymer 3 by the Click Chemistry Approach. Poly[styrene-*r*-(4-propargyloxystyrene)] **(3)** (0.11 g, 1×10^{-4} mol), the corresponding azide (4.23×10^{-4} mol), $Cu(PPh_3)_3Br$ (0.01 g, 2.37×10^{-5} mol), and DIPEA (0.06 g, 4.78×10^{-4} mol) were dissolved in dioxane (15 mL). The mixtures were stirred at room temperature for 3 days. The solutions were concentrated, precipitated in ethanol, and later on dried at 50 °C under vacuum overnight. The modified materials were obtained as solids. Yield: 80−95%.

Characterization of 3-a. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.55 (br, 1H); 7.07 (br, 2H); 6.57 (br, 3H); 5.12 (br, 2H); 4.32 (br, 2H); 4.06 (br, 2H); 3.57 (br, 1H); 3.15−3.11 (br, 2H); 2.45 (m, 1H); 2.31 (t, 2H); 1.91 (m, 3H); 1.89−1.39 (m, 15H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 173.2, 156.27, 145.22, 144.47, 137.94, 127.9, 125.5, 122.29, 114.11, 64.00, 62.20, 56.33, 50.20, 40.32, 40.17, 38.43, 34.53, 34.02, 30.10, 28.69, 28.39, 26.10, 25.37, 24.65. IR (KBr): ν (cm^{-1}) = 3059−3025 (ν CH Ar), 2919 ($\nu_{s,as}$ CH_2), 1727 (ν COO), 1602 (ν C=C Ar), 1584 (−N=N−), 1509 (ν C=C Ar), 1451 (δ CH_2), 1303 (ν CN), 1237 (ν CO), 757, 699 (δ CH Ar). Anal. Calcd for $[C_{9.9}H_{10.1}O_{0.3}N_{0.3}S_{0.2}]$: C, 76.68%; H, 6.93%; N, 3.18%; S, 4.84%. Found: C, 79.64%; H, 6.84%; N, 2.68%; S, 4.77.

Characterization of 3-b. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.77 (s, 1H), 7.58 (br, 1H), 7.05 (br, 5H), 6.57 (br, 6H), 5.57 (s, 2H), 5.10 (br, 2H), 4.58 (br, 2H), 4.32 (br, 2H), 4.18 (br, 2H), 3.96 (br, 3H), 3.93 (br, 3H), 1.82 (br, CH), 1.42 (br, CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 156.12, 154.75, 153.64, 148.36, 145.22, 144.26, 139.76, 127.57, 125.56, 122.39, 114.30, 110.16, 108.23, 68.17, 66.21, 56.44, 56.33, 50.15, 43.97, 40.36, 30.02, 28.36, 26.02, 25.07. IR (KBr): ν (cm^{-1}) = 3082−3025 (ν CH Ar), 2922 ($\nu_{s,as}$ CH_2, CH_3), 1750 (ν COO), 1601 (ν C=C Ar), 1583 (ν -N=N−), 1524 ($\nu_{s,as}$ −N=O), 1509 (ν C=C Ar), 1452 (δ CH_2), 1221 (ν CO), 757−698 (δ CH Ar). Anal. Calcd for $[C_{10.1}H_{9.8}O_{0.9}N_{0.4}]$: C, 80.15%; H, 6.45%; N, 4.08%. Found: C, 82.62%; H, 7.12%; N, 1.97%.

Characterization of 3-c. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.75 (br, 1H), 7.48 (s, 1H), 7.08 (br, 4H), 7.02 (s, 1H), 6.57 (br, 6H), 5.57 (br, 2H), 5.09 (br, 2H), 4.59 (br, 2H), 4.50 (br, 1H), 4.23 (br, 2H), 4.00 (s, 3H), 3.95 (s, 3H), 3.70 (s, 1H), 2.45 (br, 2H), 1.82 (br, CH), 1.43 (br, CH_2), 1.29 (br, 4H). ^{13}C NMR (500

MHz, $CDCl_3$): δ (ppm) = 155.89, 155.48, 153.69, 148.15, 145.66, 114.20, 139.71, 128.50, 127.97, 127.29, 125.63, 125.46, 114.28, 109.92, 108.23, 63.87, 61.77, 56.40, 52.93, 48.01, 45.92, 44.29, 40.34, 31.56, 30.84, 29.78, 28.34, 27.68, 22.63, 14.16, 14.08. IR (KBr): ν (cm^{-1}) = 3291 (ν NH), 3081−3025 (ν CH Ar), 2921 ($\nu_{s,as}$ CH_2, CH_3), 1733 (ν COO, NHCOO), 1601 (ν C═C Ar), 1583 (ν −N═N−), 1523 ($\nu_{s,as}$ −N═O), 1509 (ν C═C Ar), 1452 (δ CH_2), 1329 (ν_s NO), 757−698 (δ CH Ar). Anal. Calcd for [$C_{10.6}H_{10.7}O_{0.9}N_{0.5}S_{0.1}$]: C, 77.16%; H, 6.49%; N, 4.65%; S, 2.13%. Found: C, 67.54%; H, 7.23%; N, 6.2%; S, 1.98%.

Characterization of 3-d. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.75 (br, 1H), 7.68 (s, 1H), 7.05 (br, 4H), 7.01 (s, 1H), 6.51 (br, 6H), 5.49 (br, 3H), 5.09 (br, 2H), 4.51 (br, 2H), 3.94−3.91 (br, 6H), 3.88 (s, 2H), 3.57 (br, 4H), 3.53 (br, 2H), 3.37 (br, 2H), 1.82 (br, CH), 1.42 (br, CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 156.33, 156.01, 153.51, 148.21, 145.3, 139.99, 138.0, 128.0, 125.64, 125.48, 123.78, 114.20, 110.65, 108.24, 70.51, 70.24, 69.92, 69.44, 63.55, 62.15, 56.45, 56.40, 50.28, 40.98, 40.20. IR (KBr): ν (cm^{-1}) = 3349 (ν NH), 3082−3025 (ν CH Ar), 2922 ($\nu_{s,as}$ CH_2, CH_3), 1727 (ν COO, NHCOO), 1601 (ν C═C Ar), 1582 (ν −N═N−), 1522 ($\nu_{s,as}$ −N═O), 1510 (ν C═C Ar), 1452 (δ CH_2), 1329 (ν_s NO), 1262 (ν CO), 757−698 (δ CH Ar). Anal. Calcd for [$C_{10.2}H_{10.1}O_{1.1}N_{0.6}$]: C, 77.58%; H, 6.39%; N, 4.88%. Found: C, 73.46%; H, 6.5%; N, 3.4%.

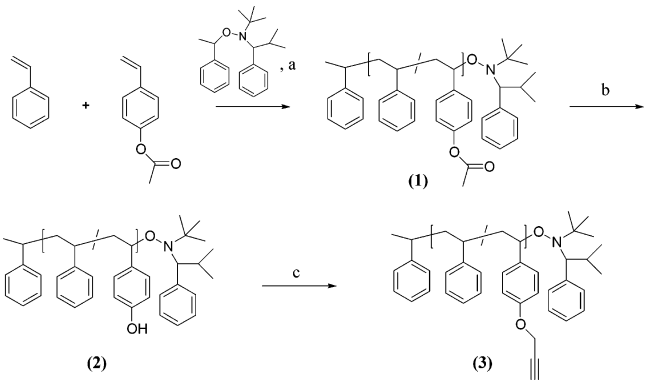
Characterization of 3-e. ^{1}H NMR ($CDCl_3$): 9.91 (s, 1H); 7.71 (s, 1H); 7.50 (d, 2H); 7.27 (s, 1H); 7.07 (d, 2H); 7.05 (br, 4H); 6.54 (br, 6H); 5.44 (s, 2H); 5.07 (br, 2H); 3.90 (s, 3H); 3.87 (s, 3H); 1.82 (br, 1H); 1.45 (br, 2H). ^{13}C NMR ($CDCl_3$): 156.12, 153.49, 152.87, 148.43, 145.78, 144.32, 138.52, 138.52, 136.85, 133.36, 127.92, 127.40, 125.59, 121.46, 119.59, 114.58, 114.16, 111.05, 108.31. IR (KBr): ν (cm^{-1}) = 3367 (ν NH), 3081−3025 (ν CH Ar), 2921 ($\nu_{s,as}$ CH_2, CH_3), 1740 (ν COO, NHCOO), 1602 (ν C═C Ar), 1582 (ν -N═N−), 1523 ($\nu_{s,as}$ −N═O), 1510 (ν C═C Ar), 1452 (δ CH_2), 1330 (ν_s NO), 1278 (ν CO), 757−698 (δ CH Ar). Anal. Calcd for [$C_{9.9}H_{8.8}O_{0.8}N_{0.6}$]: C, 80.62%; H, 5.90%; N, 5.18%. Found: C, 79.46%; H, 8.16%; N, 2.42%.

Characterization of 3-f. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.65 (br, 1H); 7.04 (br, 2H); 6.57 (br, 3H); 5.11 (br, 2H); 4.81 (br, 1H); 4.39 (br, 2H); 3.13 (br, 2H); 2.07 (br, 2H); 1.83 (br, 1H), 1.46 (br, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 156.24, 156.07, 145.24, 144.60, 137.9, 127.8, 125.58, 122.83, 114.14, 79.5, 62.11, 47.59, 40.43, 39.58, 37.33, 30.69, 28.37. IR (KBr): ν (cm^{-1}) = 3419 (ν NH), 3059−3025 (ν CH Ar), 2921 ($\nu_{s,as}$ CH_2, CH_3), 1710 (ν COO, NHCOO), 1601 (ν C═C Ar), 1584 (ν −N═N−), 1508 (ν C═C Ar), 1451 (δ CH_2), 1365 (δ $C(CH_3)_3$), 1243 (ν CO), 757−698 (δ CH Ar). Anal. Calcd for [$C_{9.2}H_{9.1}O_{0.3}N_{0.4}$]: C, 84.33%; H, 6.94%; N, 4.7%. Found: C, 83.25%; H, 3.68%; N, 3.68%.

Characterization of 3-g. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.55 (br, 1H); 7.30 (m, 1H); 7.26 (br, 2H); 7.07 (br, 2H); 6.57 (br, 3H); 5.57 (br, 2H); 5.08 (br, 2H); 1.83 (br, 1H); 1.43 (br, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 156.18, 145.24, 138.1, 132.14, 131.89, 129.51, 128.71, 127.95, 125.63, 122.06, 114.22, 62.10, 53.88, 43.9, 40.40. IR (KBr): ν (cm^{-1}) = 3058−3024 (ν CH Ar), 2919 ($\nu_{s,as}$ CH_2), 1601 (ν C═C Ar), 1583 (ν −N═N), 1509 (ν C═C Ar), 1451 (δ CH_2), 1232 (ν CO), 748−698 (δ CH Ar). Anal. Calcd for [$C_{9.1}H_{8.1}O_{0.1}N_{0.3}S_{0.1}$]: C, 85.85%; H, 6.37%; N, 3.63%; S, 2.77%. Found: C, 82.29%; H, 6.58%; N, 3.14%; S, 2.67%.

Characterization of 3-h. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.70 (br, 1H); 6.91 (br, 2H); 6.45 (br, 3H); 4.97 (br, 2H); 4.12 (br, 2H); 3.76 (br, 2H); 3.49 (br, 10H); 2.41 (br, 3H); 1.71 (br, 1H), 1.30 (br, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 155.63, 145.3, 144.26, 138.0, 127.96, 125.64, 122.67, 114.35, 70.51, 70.48, 69.15, 68.96, 63.55, 62.27, 58.40, 55.90, 40.43. IR (KBr): ν (cm^{-1}) = 3286 (ν NH), 3082−3025 (ν CH Ar), 2921 ($\nu_{s,as}$ CH_2), 1601 (ν C═C Ar), 1583 (ν −N═N−), 1509 (ν C═C Ar), 1452 (δ CH_2), 1263 (ν CO), 758−698 (δ CH Ar). Anal. Calcd for [$C_{9.1}H_{9.1}O_{0.44}N_{0.4}$]: C, 83.05%; H, 6.91%; N, 4.68%. Found: C, 87.13%; H, 7.00%; N, 4.22%.

Scheme 1. Synthesis of the Copolymer Poly(styrene-*r*-4-propargyloxystyrene) (3) by NMRP and Subsequent Polymer Analogous Reactions: (a) NMRP, Nitroxide Adduct, Acetic Anhydride, 120 °C; (b) $NH_2NH_2 \cdot H_2O$, Dioxane, RT; (c) Propargyl Bromide, DMF, RT



Results and Discussion

As a starting precursor polymer, random poly[styrene-*r*-(4-acetoxystyrene)] **(1)** was synthesized by NMRP using 2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide as initiator (see Scheme 1). This nitroxide adduct developed by Hawker et al.[31] allows to polymerize a wide variety of monomers in a controlled fashion, as acrylates, styrene derivatives, acrylamides, 1,3-dienes, and so on, and it also allows to perform the polymerization under relative mild conditions. The most striking difference of the chosen structure is the presence of a hydrogen atom on one of the α-carbons, in contrast to the two quaternary α-carbons present in the traditional TEMPO and other nitroxides. The initiator was synthesized following the experimental conditions described in the literature above. It is well-known that many styrene derivatives can be polymerized by NMRP keeping the control over the reaction. One example is 4-acetoxystyrene, which is a good precursor for hydroxyl groups in position 4, ready for further modification. Thus, the monomers styrene and 4-acetoxystyrene were mixed in a given feed ratio (9:1) with acetic anhydride together with the initiator, and the polymerization was carried out in the bulk under an inert atmosphere at 120 °C similar as described previously.[30,32] The purification of the polymer was performed by subsequent precipitations in ethanol. The reactivity ratios of styrene and 4-acetoxystyrene (1.02 and 0.80, respectively) indicate that the final polymer should exhibit a structure with high tendency to randomness. The overlapping of the signals in the CH, CH_2 region of the ^{13}C NMR, however, did not allow to establish definitive conclusions about the microstructure of the polymer. Our polymer was obtained with a narrow molar mass distribution and a polydispersity index of ∼1.17 ($\bar{M}_n$ = 26 700 g/mol). The calculated molar mass based on the obtained conversion was on the order of 27 000, which indicates that the polymers were obtained with a good control of the molar mass and PDI. This result is in accordance with previous experiments performed on NMRP in our laboratories.[33]

Later on, the hydrolysis of the acetyl group was carried out under basic conditions to provide free phenolic groups (see Scheme 1, b). This reaction led to poly[styrene-*r*-(4-hydroxystyrene)] **(2)**. A number of procedures have been described for such an hydrolysis reaction using different bases.[34,35] Comparative studies have demonstrated that for the removal of the acetyl groups reactions with hydrazine hydrate are better than those with NaOH, as hydrazine monohydrate often provides deacetylated materials free of any side reactions which might lead to cross-linked products. For this reason hydrazine monohydrate

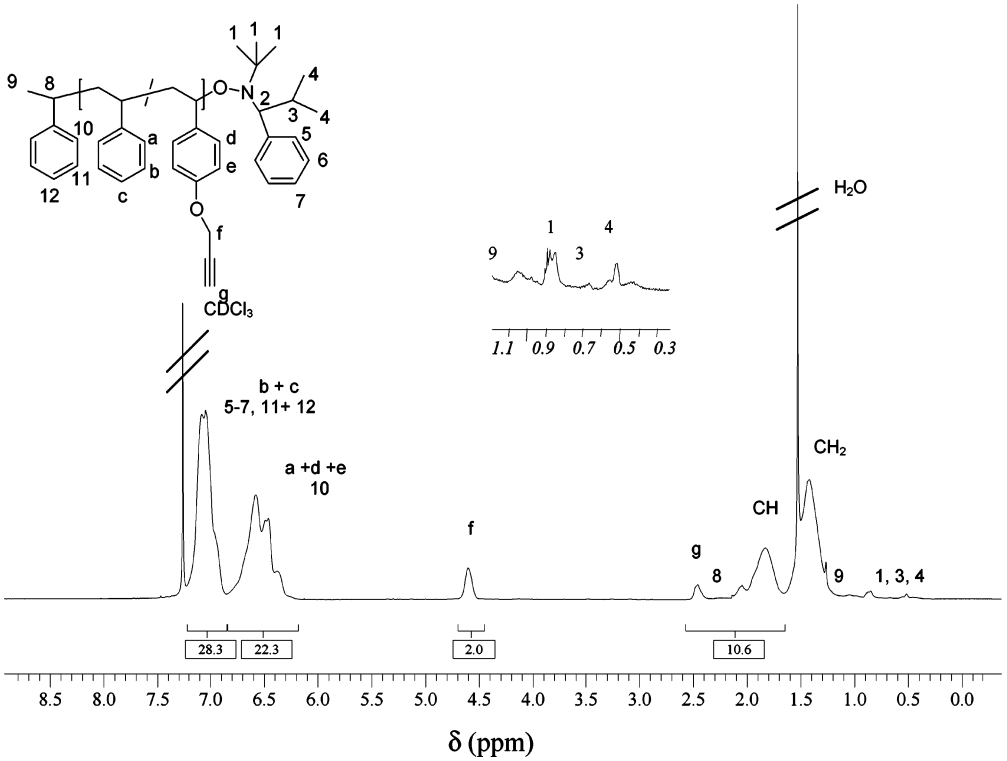


Figure 1. ^{1}H NMR spectrum of poly[styrene-*r*-(4-propargyl-oxystyrene)] (**3**) in $CDCl_3$.

was chosen as hydrolytic agent. The quantitative removal of the acetyl group can be observed in ^{1}H NMR ($CDCl_3$) by the disappearance of the peak corresponding to the acetyl group at 2.27 ppm and by the appearance of a broad signal at 4.80−4.25 ppm corresponding to the hydroxy group. These results are in accordance with previous experiments in our laboratories.[30]

In a second step, the alkyne-modified polymer **3** was obtained by treatment of **2** with propargyl bromide following the conditions described in the literature[36] (see Scheme 1, c). In the ^{1}H NMR spectra of **2** can be observed featuring the propargyl group a peak at $\delta = 2.46$ ppm (C≡C−H, 1H) and another at $\delta = 4.60$ ppm (O−CH_2−C≡C−H, 2H). The integration of both signals with respect to the aromatic groups indicates the quantitative character of the reaction. From the relative integration between the aromatic units from styrene and the propargyl group a ratio 89/11 was obtained, which is in accordance with the monomer ratio in the feed of the starting polymer **1** (see Figure 1). In the ^{13}C NMR spectra the signals at $\delta_1 = 55.9$, $\delta_2 = 79.0$, and $\delta_3 = 75.2$ ppm corresponding to the three atoms of the propargyl group (−C_1−C_2≡C_3−), respectively, demonstrate the success of the reaction. Additionally is shown an enlargement of the area 1.1−0.3 ppm of the ^{1}H NMR spectra, in which protons corresponding to nitroxide initiator (TPPA) fragments included in the polymer are exhibited.

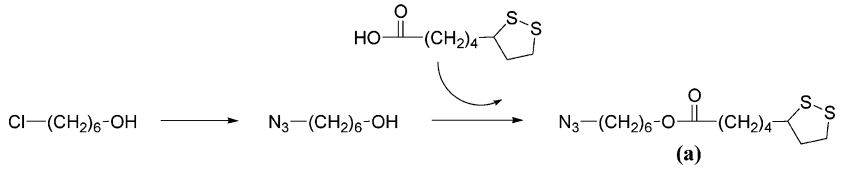
Both modified copolymers **2** and **3** were also characterized using GPC, which revealed $\bar{M}_n = 26\,000$ g/mol and $\bar{M}_n = 27\,000$ g/mol, respectively, and PDI = 1.20 and 1.21. Comparing these values vs $\bar{M}_n = 27\,100$ g/mol and PDI = 1.17 of the starting material **1**, we can see that the narrow molar mass distribution was retained, which points to that the polymer analogous reactions proceeded efficiently. Copolymer **3** was thought to be a good platform for further modification of the propargyl group by means of click reactions (1,3-dipolar Cu-catalyzed cycloaddition reactions) as pendant terminal alkynes are suitable for reacting with azides in the presence of Cu(I) catalyst.

This approach constitutes a modular synthesis which allows the introduction of a variety of functional groups starting from a rather easily available copolymer. Moreover, the mentioned intended cycloaddition reactions work with high conversions, and they are selective toward functional groups; hence, one can carry out a tailor-made functionalization of the polymers depending on the polymer application. Several functional azides were used to introduce a variety of functionalities in the materials. Some of them were synthesized for this work, and others could be purchased.

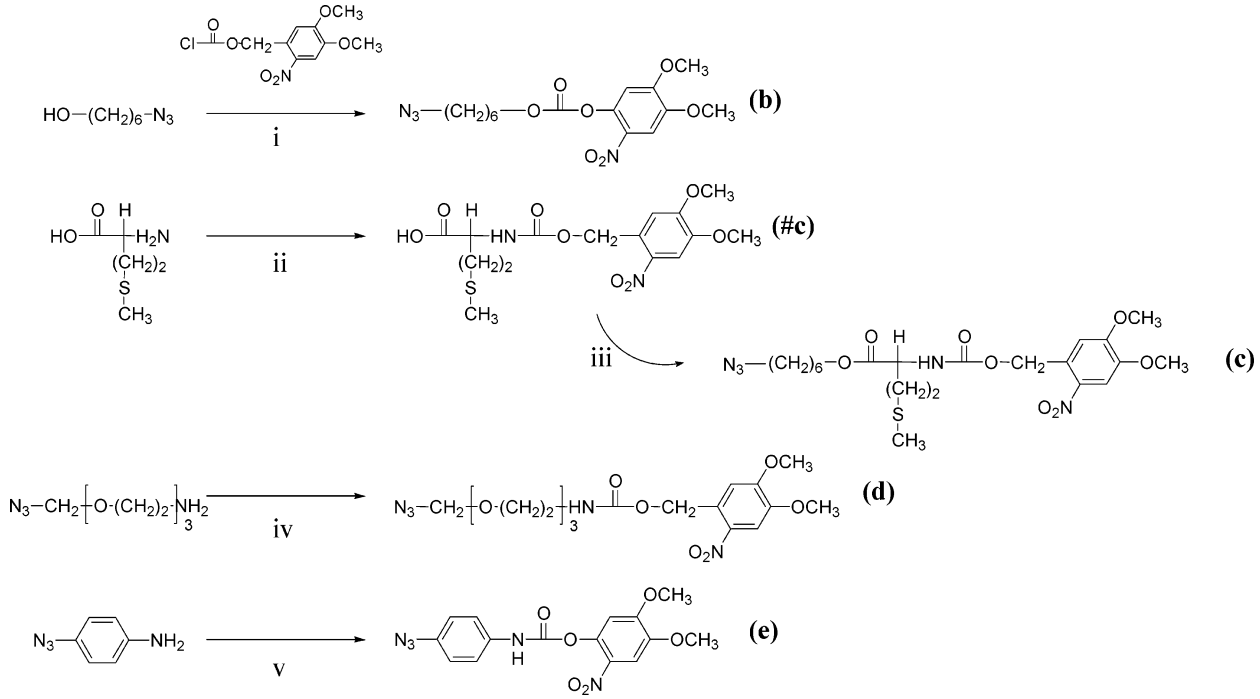
As outlined earlier, this work is focused on the preparation of polymers adequate for surface patterning, preferably onto gold substrates. Thus, some azides were designed for this purpose allowing, e.g., the incorporation of a sulfide derivative anchoring group. In a previous paper we reported a family of side-chain polymers obtained by free radical polymerization in which lipoic units were introduced by copolymerization of specially designed monomers for covalent anchoring onto gold.[26] Now, 5-[1,2]dithiolan-3-yl-pentanoic acid 6-azidohexyl ester **(a)** was obtained by esterification of lipoic acid and 6-azido-1-hexanol (see Scheme 2). The esterification process was performed in presence of DCC and DMAP, which provided the final ester compound in high yields (90%) and under mild conditions. The reaction conditions used for the esterification were reported in the previous work mentioned above. The precursor 6-azido-1-hexanol was synthesized from 6-chloro-hexanol and NaN_3 following a procedure described in the literature.[37]

In order to obtain photolabile polymers for patterning applications, azide **b** was synthesized from 6-chlorohexanol and 2-nitroveratryl chloroformiate as depicted in Scheme 3, i. An azide derivative from an aminoacid was synthesized later on following the route as depicted in Scheme 3, ii and iii. Amino acids are well-known not only because they are constituents of

Scheme 2. Synthesis of the Azide 5-[1,2]Dithiolan-3-yl-pentanoic Acid 6-Azidohexyl Ester (a)



Scheme 3. Synthesis of Photolabile NVOC-Derivative Azides



proteins and typical biological polymers but also because they are useful substances for chiral auxiliaries and building blocks, and they are used in organic synthesis for the incorporation of a variety of chemical and biochemical functions. This aroused the interest in the design of an azide including both a photolabile and an anchoring group for gold, enabling the incorporation of two specific properties in one step. For this purpose the aminoacid methionine was selected. Although S−S is reported to be a more effective anchoring group, anchoring groups for gold containing the moiety methyl sulfide CH_3-S- have been also described.[38] The amino group from methionine enables an easy protection by the photolabile unit of choice, nitroveratryl oxycarbonyl (NVOC) in a first step, and the carboxylic group remains as a functional branch in which an azide moiety can be easily incorporated (see Scheme 3, iii). This group was esterified with 6-azido-1-hexanol which provided the multifunctional azide 2-(4,5-dimethoxy-2-nitrobenzyloxycarbonylamino)-4-methylsulfanylbutyric acid 6-azidohexyl ester, depicted as **c**. The conditions used for the esterification were analogous as those used for the synthesis of azide **a**.

Another photoactive azide having a longer spacer and thus a more flexible structure was obtained from the reaction of 11-azido-3,6,9-trioxane undecane-1-amine and 2-nitroveratryl chloroformiate (see Scheme 3, iv, depicted as **d**. From 4-azidoaniline and nitroveratryl chloroformiate (Scheme 3, v) the azide (4-azidophenyl)carbamic acid-4,5-dimethoxy-2-nitrobenzyl ester **(e),** as described in the Experimental Part, also was synthesized for this work.

The nitroveratryl group has been used in previous investigations in which comb-type terpolymers were obtained by free radical polymerization and later on were used for selective patterning of ultrathin films anchored onto silicon wafers.[24] Selective irradiation in presence of a mask freed amino groups which were used for the attachment of gold colloids or nanoelements.[25,39] In addition to the mentioned designed compounds, some commercially available azides with interesting properties were also used for our purposes. One of them was 3-azidopropylcarbamic acid *tert*-butyl ester. The ^{t}butyloxycarbonyl group (^{t}BOC) is well-known as a protective group for OH and amino functions. This group is extensively used in phenolic polymers for lithographic and photoresist applications, and it allows the release of the functional groups after irradiation in presence of a photoacid generator (PAG). These molecules (PAG) provide strong acidic species (H^+) after irradiation with UV light which promote the release of the protecting group after a postbaking process. Although the yield in the deprotection of NH_2 is not so high as for OH groups, NH_2 groups can also be obtained in moderate yields in the presence of triphenylsulfonium triflate as we have been recently investigating.[40] Azide azidomethylphenyl sulfide **(g)** was also chosen in order to study the anchoring capacity of this moiety to gold substrates as well as 11-azido-3.6.9-trioxane undecane-1-amine **(h)** which supplies directly free amino functionalities in polymer **3-h**.

The 1,3-dipolar Cu-catalyzed coupling of azides to alkynes is often performed using mild conditions. Some well-known catalysts systems for the performance of these cycloaddition reactions are $Cu(I)\cdot P(OEt_3)$/DIPEA, $CuSO_4\cdot 5H_2O$/sodium ascorbate, CuI/DIPEA, or CuI/DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Because of solubility reasons, $Cu(PPh_3)_3Br$/DIPEA was chosen as catalyst system and dioxane as reaction media. The reaction mixtures were stirred at room temperature for 3 days under a nitrogen atmosphere, and by precipitation in ethanol

Table 1. Most Relevant Properties of the Different Copolymers

polymer	calcd $\bar{M}_n$ (g/mol)	conv[a] (%)	$\bar{M}_n$ (g/mol)	PDI	T_g (°C)	$T_{1\%loss}$ (°C)	$T_{10\%loss}$ (°C)
1	27 100	90	26 400	1.17	105	256	355
2	26 000	95	27 900	1.20	110	206	362
3	27 000	95	27 000	1.21	99	231	396
3-a	35 500	95	37 800	1.44	72	215	342
3-b	35 000	78	34 000	1.24	92	213	344
3-c	37 400	75	31 800	1.32	75	155	287
3-d	38 200	95	27 600	1.39	77	83	267
3-e	35 300	85	30 200	1.25	110	210	280
3-f	32 100	94	30 700	1.23	131	196	305
3-g	31 300	95	29 600	1.29	78	152	266
3-h	32 300	95	28 300	1.23	107	313	368

[a] Calculated according to ^{1}H NMR integration. According to the accuracy of the NMR technique, conversions higher than 95% cannot be confirmed.

the desired materials were obtained without further purification steps in high yields (70−95%) (see Table 1). Their chemical structures are shown in Scheme 4.

In Figure 2a the FTIR spectrum of polymer **3** is shown, where the bands corresponding to the propargyl group can be seen at 2092 cm^{-1} (C≡C) and 3013 cm^{-1} (≡C−H). In Figure 2b the spectrum of a modified material **3-a** is shown, in which one can confirm that these bands disappear. Together with the spectrum of **3-a**, the spectrum of the precursor azide is shown as a dashed line. The absence of N_3 band in **3-a** FTIR is observed, but the presence of bands at 1239 and 1169 cm^{-1} characteristic for the azide are visible, indicating that the incorporation of the azide was successful. Some significant bands of the polymers are indicated in the represented spectra and more in detail for all the materials in the Experimental Part.

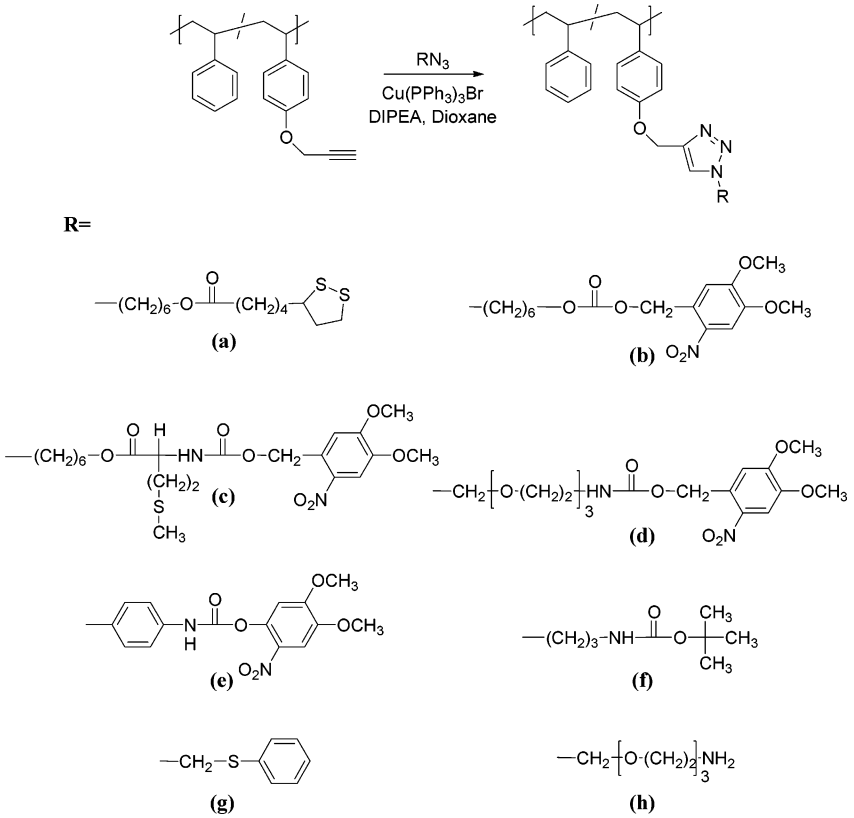
The effectiveness of the reactions was proven also by ^{1}H NMR and ^{13}C NMR. In Figure 3 the ^{1}H NMR spectra of polymer **3-d** are shown. Two signals are significant in the determination of the new materials: one is a broad peak found at around 5 ppm corresponding to the $-CH_2-$ group bonded to the triazol ring, and the other is the peak appearing at around 7.5 ppm corresponding to the aromatic proton of the triazol ring. The remaining signals in the spectra could be fully assigned and are in correspondence with the proposed polymer structures.

In the example shown no peak corresponding to the propargyl group is observed, which indicated that the reaction proceeded in this case quantitatively according to the NMR accuracy. A yield ≥95% was assumed to calculate the theoretical molar masses of the final materials in the cases in which no remaining of propargyl group was detected.

Finally, in ^{13}C NMR spectra of polymer **3-d** (see Figure 4) the absence of peaks at $\delta_1 = 55.9$, $\delta_2 = 79.0$, and $\delta_3 = 75.2$ ppm corresponding to the propargyl group was observed vs the appearance of peaks designed as e, f, g assigned to the modified polymer as specific of the triazole ring and adjacent $-CH_2-$ group.

Characterization of the obtained polymers by a combination of spectroscopic and chromatographic techniques demonstrated the efficiency of this functionalization strategy. In Table 1 the main properties of the copolymers are summarized. At first, it is interesting to observe the influence of the postmodification reaction on the molecular weight of the materials. The incorporation of the functional azides into **3** leads to an increase in the molecular weight. In most cases the obtained $\bar{M}_n$ are in accordance with the predicted $\bar{M}_n$ calculated for each polymer. Small increases in the polydispersity indexes are in general observed, but they remain mostly below 1.3 (PDI value). Polymer **3-a** exhibits a higher increase in the polydispersity index (up to 1.44) with bimodal distribution (see Figure 5), and surprisingly the obtained molar mass was higher than expected. It is possible that the complexation affinity of the Cu(I) catalyst $Cu(PPh_3)Br$ to the disulfide promoted the formation of small amount of polymeric complexes, providing higher increase of

Scheme 4. Postmodified Polymers by Click Reactions with Functional Azides



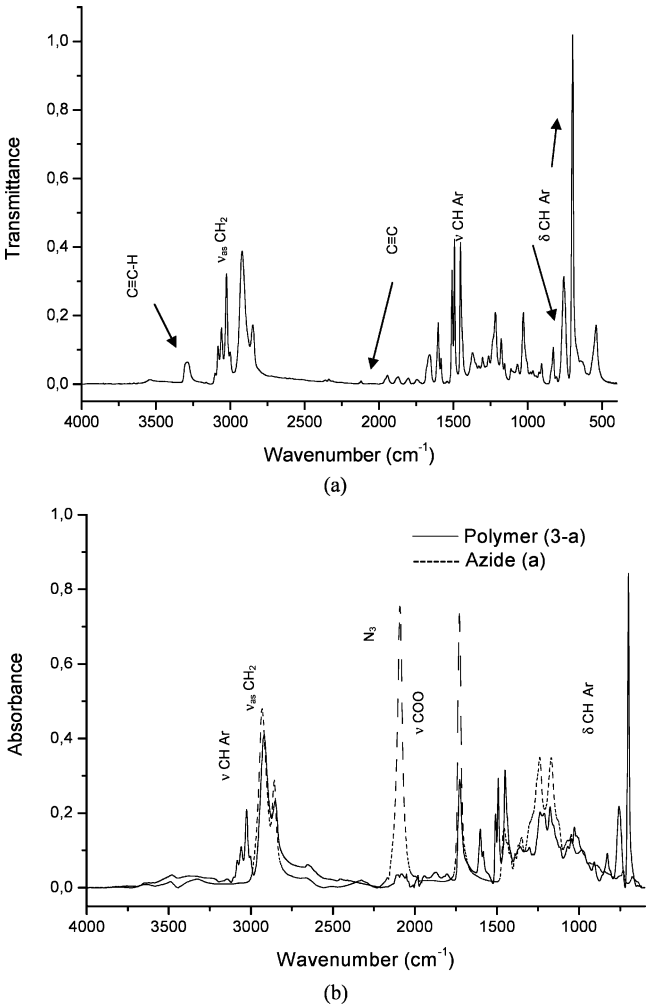


Figure 2. FTIR spectra of polymers: **3** shown in (a) and **3-a** shown in (b).

the polydispersity in the modified material as well as $\bar{M}_n$ higher than expected due to a small amount of chain combinations. Polymers **3-c** and **3-d** exhibited polydispersity indexes of 1.32 and 1.39, and the difference of $\bar{M}_n$ between expected and obtained molar masses was slightly higher. Glaser analogous coupling reactions could be a reason for this small increases in the polidispersity.[41] In Figure 5 several representative GPC curves of the copolymers are shown in which the mentioned effects can be observed.

Thermal properties of the materials were studied by DSC and TGA. All the materials exhibited a glassy amorphous behavior. Polymer **1** displayed a glass transition of 105 °C, which increased up to 110 °C after the hydrolysis of the acetyl group. Interactions among OH groups are probably the reason for this increase. These interactions are again eliminated with the incorporation of the propargyl group which as expected provided a glass transition (99 °C) slightly lower than **1**.

For the modified materials a general decrease in the glass transition was observed. Polymers **3-a**, **3-d**, **3-c**, and **3-g** exhibited glass transitions around 75−78 °C. Polymer **3-b** exhibited a glass transition of 92 °C. In comparison with polymer **3-d** this increase can be explained by the shortening of the alkyloxy chain. For polymer **3-g** a glass transition of 107 °C was obtained. Polar interactions between amine groups can be responsible for this rather high T_g, which becomes even higher for polymer **3-e**, up to 110 °C, as a consequence of the aromatic ring introduced. The highest glass temperature is observed in the case of copolymer **3-f**, with 131 °C, due to the presence of the bulky ^{t}BOC group.

On average, $T_{10\%\ loss} > 340$ °C was found for most of the polymers. Exceptions are **3-f** with $T_{10\%\ loss} = 305$ °C and polymers **3-d**, **3-e**, **3-c**, and **3-g** with $T_{10\%\ loss}$ between 260 and 280 °C due to the labile protecting groups. $T_{1\%\ loss}$ is in general higher than 150 °C, with the exception of polymer **3-d** in which the small weight loss at 83 °C could be due to the presence of traces of solvents. In general, we can say that the thermal stability of the obtained materials is adequate for the use in thin functional films.

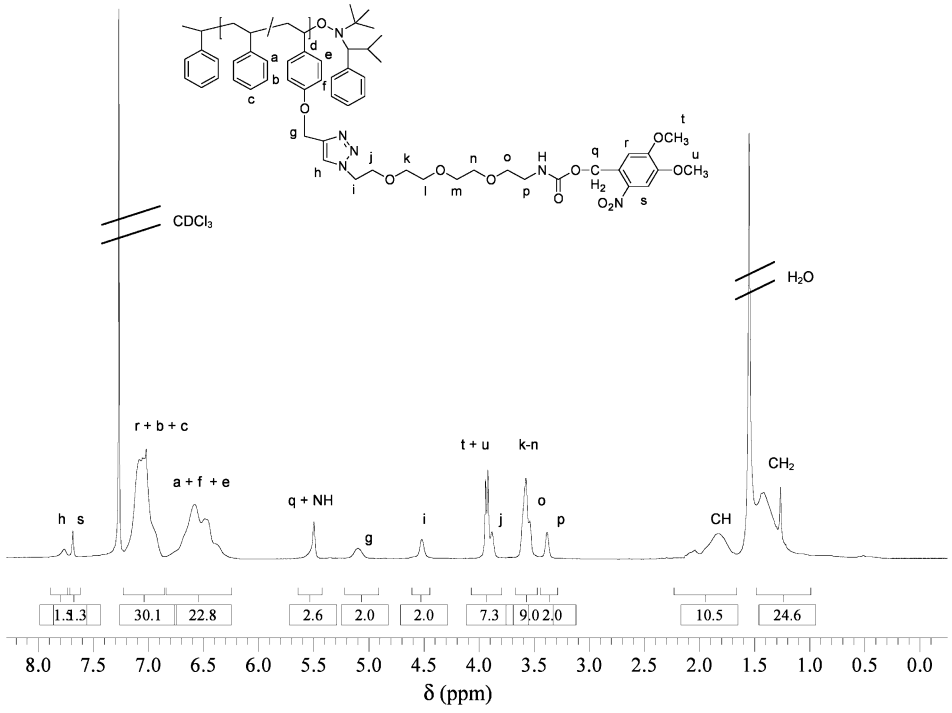


Figure 3. ^{1}H NMR spectra of the copolymer **3-d**.

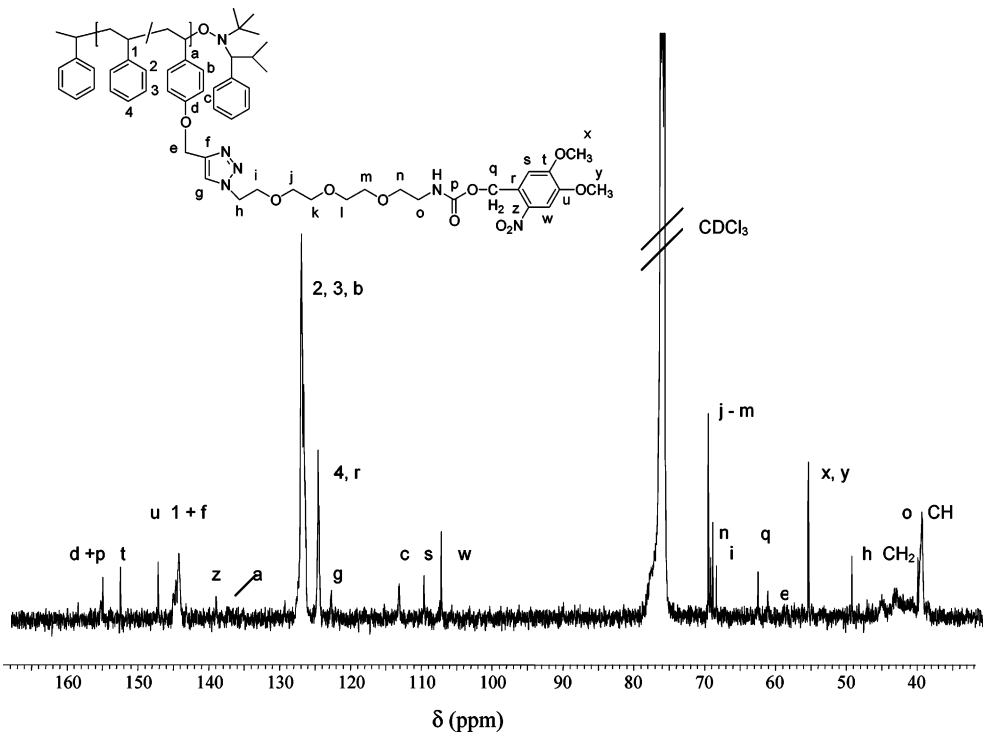


Figure 4. ^{13}C NMR of polymer **3-d** in $CDCl_3$.

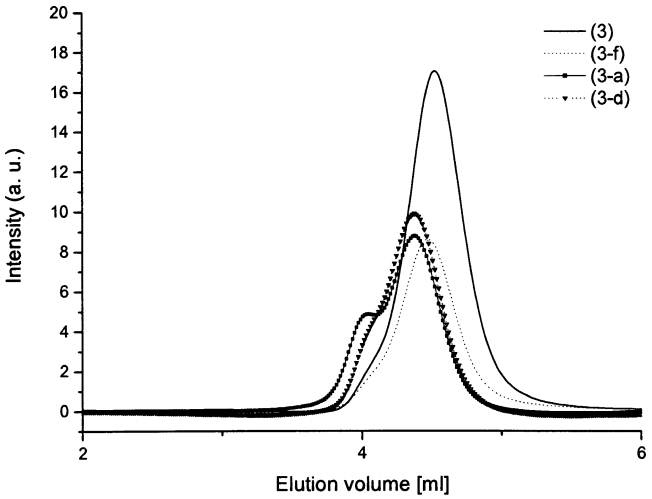


Figure 5. GPC traces of some of the obtained polymers in $CHCl_3$.

Conclusions

A random copolymer containing styrene and 4-acetoxystyrene units was synthesized by nitroxide-mediated polymerization (NMRP) with a narrow molecular weight distribution. Furthermore, the polymer was modified by two analogous polymer reactions and subsequent Cu(I) catalyzed 1,3-dipolar cycloadditions to get a family of functional polymers with specific properties: capability for photopatterning with functional groups and/or of covalent anchoring onto gold substrates. Analysis of the materials by ^1H NMR, IR, and GPC revealed that the click chemistry approach is applicable as an effective postfunctionalization strategy for the preparation of side-functionalized polymers. Synthesis of terpolymers by simultaneous or cascade polymer analogous reactions and the study of the potential of these materials in nanotechnology and lithographic patterning are currently being investigated in our laboratories.

Acknowledgment. We want to gratefully acknowledge G. Adam for the performance of the FTIR spectra, P. Treppe for the performance of the GPC, M. Molenda for her help with the synthetic work, and S. Fleischman for his useful comments. We also want to acknowledge the Deutsche Forschungsgemeinschaft (DFG) in the frame of SFB287 and FOR355 for the financial support.

References and Notes

(1) Langer, R.; Tirrel, D. A. *Nature* **2004**, *428*, 487.
(2) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 12, 3689−3746.
(3) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(4) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3668.
(5) Chiefari, J.; Rizzard, E. *Handbook of Radical Polymerization*; Matyjaszweski, K., Davis, T. P., Eds.; Wiley-Interscience: Hoboken, NJ, 2002; p 621.
(6) Percec, V.; Popov, A. V.; Ramirez-Castillo, E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 287−295.
(7) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491−1546.
(8) Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H. W. In *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, 1998; Vol. 3.
(9) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847−1876. Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139−4176.
(10) Uhrich, K. E.; Cannizaro, S. M.; Langer, R. S.; Shakesheff, K. M. *Chem. Rev.* **1999**, *99*, 3181−3198. Lee, K. Y.; Mooney, D. J. *Chem. Rev.* **2001**, *101*, 1869−1880.
(11) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823−1848.
(12) McQuada, D. T.; Pullan, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574.
(13) Liebert, T.; Hänsch, C.; Heinze, T. *Macromol. Rapid Commun.* **2006**, *27*, 208−213.
(14) Ladmiral, V.; Mantovani, G.; Clarkson, G. J.; Cauet, S.; Irwin, J. L.; Haddleton, D. M. *J. Am. Chem. Soc.* **2006**, *128*, 4823−4830.
(15) van Steenis, D. J. V. C.; David, O. R. P.; van Strijdonck, G. P. F.; van Maarseveen, J. H.; Reek, J. N. H. *Chem. Commun.* **2005**, 4333−4335.
(16) Diaz, D. D.; Punna, S.; Holzer, P.; McPherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4392−4403.

(17) Helms, B.; Mynar, J. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020−15021.
(18) Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russel, T. P.; Wu, P.; Fokin, V. V. *Macromolecules* **2005**, *38*, 3663−3678.
(19) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928−3932.
(20) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599.
(21) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.
(22) Old example of the reacion: Huisgen, R.; Szeimies, G.; Möbius, L. *Chem. Ber.* **1967**, *100*, 2494−2507.
(23) Malkoch, M.; Thibault, R. J.; Drockenmuller, E.; Messerschmidt, M.; Voit, B.; Russel, T. P.; Hawker, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 14942−14949.
(24) Braun, F.; Eng, L.; Trogisch, S.; Voit, B. *Macromol. Chem. Phys.* **2003**, *204*, 1486−1496.
(25) Opitz, J.; Braun, F.; Seidel, R.; Pompe, W.; Voit, B.; Mertig, M. *Nanotechnology* **2004**, *15*, 717−723.
(26) Sieczkowska, B.; Millaruelo, M.; Voit, B. *Des. Monomers Polym.* **2005**, *8*, 629−644.
(27) Millaruelo, M.; Eichhorn, K.-J.; Sieczkowska, B.; Voit, B. *Langmuir* **2006**, *22*, 9436−9445.
(28) Millaruelo, M.; Eng, L. M.; Mertig, M.; Pilch, B.; Oertel, U.; Opitz, J.; Sieczkowska, B.; Simon, F.; Voit, B. *Langmuir* **2006**, *22*, 9446−9452.
(29) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.
(30) Messerschmidt, M.; Häussler, L.; Voit, B.; Krause, T.; Habicher, W. D. *Macromol. Symp.* **2004**, *210*, 111−120.
(31) Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **2000**, *33*, 363−370.
(32) Leuteritz, A.; Messerschmidt, M.; Voit, B.; Yin, M.; Krause, T.; Habicher, W. D. *Polym. Prepr.* **2002**, *43*, 283.
(33) Messerschmidt, M. Ph.D. Thesis, University of Dresden.
(34) Chen, X.; Jankova, K.; Kops, J.; Batsberg, W. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 627−633.
(35) Barclay, G. G.; Hawker, C. J.; Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. *Macromolecules* **1998**, *31*, 1024−1031.
(36) Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem.* **1996**, *61*, 2511−2516.
(37) Davis, B. G.; Khumtaveeporn, K.; Bott, R. R.; Jones, J. B. *Bioinorg. Med. Chem.* **1999**, *7*, 2303−2311.
(38) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103−1168.
(39) Voit, B.; Braun, F.; Loppacher, Ch.; Trogisch, S.; Eng, L. M.; Seidel, R.; Gorbunoff, A.; Pompe, W.; Mertig, M. *ACS Symp. Ser.* **2004**, *874*, 118−128. Voit, B.; Braun, F.; Gernert, M.; Sieczkowska, B.; Millaruelo, M.; Mertig, M.; Öpitz, J. *Polym. Adv. Technol.* **2006**, *17*, 691−693.
(40) Millaruelo, M.; et al. Manuscript in preparation.
(41) Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, *1*, 51−68.

MA062410Z