Tailor Made Side-Chain Functionalized Macromolecules by Combination of Controlled Radical Polymerization and Click Chemistry

Andreas Krieg,[1] *C. Remzi Becer,*[1,2,3] *Richard Hoogenboom,*[2,3] *Ulrich S. Schubert**[1,2,3]

Summary: Reversible addition-fragmentation chain transfer polymerization of trimethylsilyl-propargyl methacrylate (TMSPMA) was performed to obtain alkyne containing polymers with narrow molecular weight distributions (PDI < 1.3). Homopolymers of TMSPMA as well as random and block copolymers with methyl methacrylate were synthesized and subsequently deprotected. The obtained acetylene-functionalized polymers were further functionalized using the copper(I) catalyzed alkyne-azide cycloaddition reaction to obtain well-defined glycopolymers, grafted copolymers and anthracene-containing polymers (PDI $= 1.08$–1.28) that were characterized with GPC, MALDI-TOF mass spectrometry and ^{1}H-NMR-spectroscopy.

Keywords: click chemistry; glycopolymer; graft copolymer; reversible addition-fragmentation chain transfer polymerization; trimethylsilyl-propargyl methacrylate

Introduction

Polymers with precise and well-defined structures have been attracting great interest to fulfill particular tasks in high-tech applications, i.e. as drug delivery systems, in bio recognition or in optical devices.[1–7] Different strategies have been employed to obtain suitable designed macromolecules and, more importantly, to develop an adaptable ''universal'' backbone that can serve for carrying various functionalities.[8–11] Nowadays, the universal backbone approach can be achieved by highly efficient post-polymerization modifications, which can be the so-called ''click'' reactions,[12,13] following controlled and/or living polymerization techniques.[14,15]

Such a universal backbone polymer should consist of relatively inexpensive and easily polymerizing monomers. In addition, the resulting polymer should be sufficiently stable during the post–modification reactions. The combination of controlled radical polymerization techniques (CRP) and the so called ''click–chemistry'' seems to be a proper way to meet these demands. Controlled radical polymerization methods (nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT))[16–18] lead to well-defined polymers with desired composition and narrow molecular weight distributions.

The copper catalyzed alkyne-azide cycloaddition (CuAAC, click chemistry) represents a versatile method to modify polymers under mild conditions with a high tolerance for already existing functional groups.[19–21] In general, side-chain modifications on polymers often include the disadvantage of incomplete degrees of

[1] Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, D-07743 Jena, Germany
E-mail: ulrich.schubert@uni-jena.de
[2] Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Den Dolech 2, 5612AZ, Eindhoven, The Netherlands
[3] Dutch Polymer Institute, P.O. Box 902, 5600AX, Eindhoven, The Netherlands

functionalization. Possible reactions are limited due to the conditions that the polymers can tolerate without negative results for their properties, such as the number average molecular weight (M_n) and the polydispersity index (PDI). In this respect a reaction like the CuAAC that is running under mild conditions and in most cases leading to rather high yields represents a highly suitable solution for these problems.

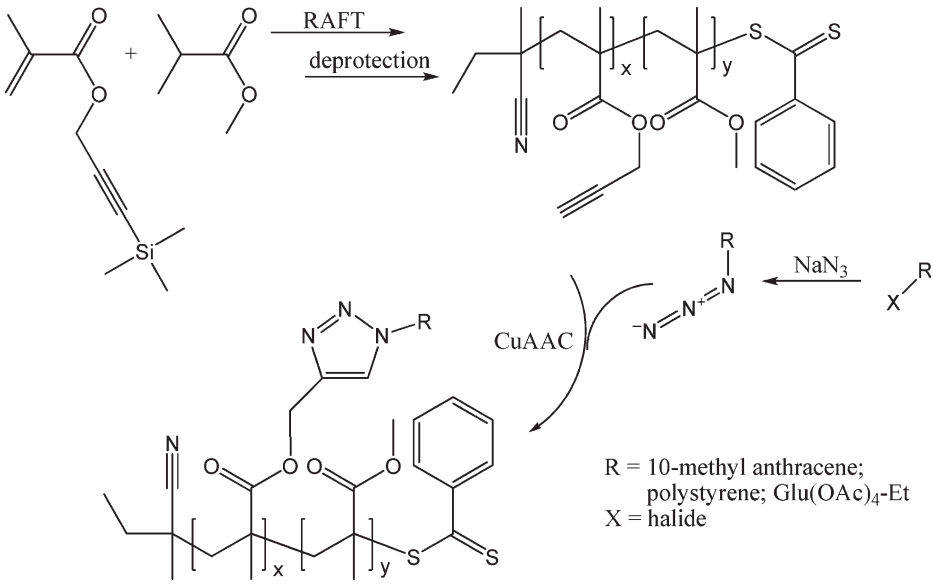
The alkyne containing monomer used in this work, trimethylsilyl-propargyl methacrylate (TMSPMA), is already known as a suitable monomer to prepare polymers that can be modified by ''click chemistry''.[22] An excellent CRP technique, in particular for methacrylate based monomers, is the RAFT technique, which we employed in this work (see Scheme 1 for an overview).[23,24]

The combination of these two powerful tools for polymer preparation enables the synthesis of macromolecules decorated with a wide range of functionalities like grafted watersoluble side chains, sugars moieties or optical active molecules. In addition, the possibility of applying automated high-throughput preparation methods to prepare polymer backbones with RAFT,[25] followed by the fast and tolerant CuAAC modification, will allow the easy synthesis of compound libraries for structure-property relationship studies in the future.

Experimental Part

Monomer Synthesis

Trimethylsilyl-propargyl methacrylate (TMSPMA) was synthesized following the procedure developed by Haddleton and coworkers.[22] A solution of 2.8 g of TMS-propargyl alcohol (21.8 mmol) and 4.5 mL triethyl amine (32.1 mmol, 1.5 equivalents compared to TMS-propargyl alcohol) in 30 mL diethyl ether was cooled to −20 °C while stirring. Subsequently, a solution of 2.7 mL methacryloyl chloride (28.5 mmol, 1.3 equivalents) in 15 mL of diethyl ether was added dropwise during one hour. The turbid yellow mixture was stirred at this temperature for half an hour and then allowed to reach room temperature. After



Scheme 1.
Schematic representation of the approach to functional polymers by a combination of RAFT (initiator: *N,N′*-azo-*bis*-di-isobutyronitril (AIBN); chain-transfer agent: 2-cyano-2-butyl dithiobenzoate (CBDB)) and CuAAC (copper(I) iodide; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)).

stirring at room temperature overnight, the ammonium salts were removed by filtration and the solvent was evaporated under reduced pressure.

The purification of the remaining yellow oil via a silica column (petrol ether/diethyl ether 20:1) led to 3.3 g (16.7 mmol, 76.6% yield) of TMSPMA as a clear, colorless oil.

Polymerization

For the synthesis of copolymers, TMSPMA and/or MMA were mixed in the desired ratio and dissolved in toluene with a monomer concentration of 2 M. Following the addition of the initiator (*N,N′*-azo-*bis*-di-isobutyronitril (AIBN), 0.25 eq.) and the chain transfer agent 2-cyano-2-butyl dithiobenzoate (CBDB, 1 eq.), the mixture was bubbled with argon for 30 minutes. PMMA ($M_n = 3{,}500$ Da, PDI = 1.12) was used as a macro chain transfer agent for the synthesis of **D4**. Afterwards, the solution was placed into an oil bath preheated to 70 °C and allowed to react for the desired time. After removing the solvent and redissolving the residues in tetrahydrofuran (THF), the solution was precipitated into a cold methanol/water mixture (5/1 v/v) to obtain the purified polymer.

Deprotection

The protected polymer was dissolved in THF with a concentration of 0.07 M and 1.5 equivalents of acetic acid, according to the protected alkyne functions, were added. After bubbling for 10 minutes with argon, the solution was cooled to −20 °C and a 0.2 M solution of TBAF × 3 H_2O (1.5 equivalents relative to the trimethylsilyl protection groups) was added dropwise with a syringe. After stirring for 30 min, the solution was allowed to reach room temperature and continued to stirr for additional 2 hours.

Subsequently, the mixture was passed through a short silica column to remove TBAF × 3 H_2O and, after washing the column with additional THF, the solution was concentrated under reduced pressure before precipitating the polymer into petrol ether.

Synthesis of Azide Functionalized Compounds

10-(Azidomethyl)anthracene and 1-(2-azidoethyl)-2,3,4,6-*O*-tetraacetate-*β*-D-glucopyranosid (Glu(OAc)$_4$-Et-N_3) were synthesized from 10-(bromomethyl)anthracene and 1-(2-bromoethyl)-2,3,4,6-*O*-tetraacetate-*β*-D-glucopyranosid by converting the halide functionality to an azide with sodium azide in dimethylformamide (DMF) according to a literature procedure.[26]

The azide endfunctionalized polystyrene (PS-N_3) was synthesized in a similar way using a bromine endfunctionalized polystyrene (PS-Br) that was obtained by atom transfer radical polymerization (ATRP) of styrene as previously reported.[27] The characteristic values ($M_n = 7{,}200$ Da; PDI = 1.09) did not change during the azide endfunctionalization.

CuAAC Click Reaction

The deprotected polymer, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 10% relative to alkyne functionalities) and the azide containing compound (1.05 to 1.1 equivalents azide function relative to alkyne function) were dissolved in THF and bubbled with argon for 30 min. A catalytical amount of copper(I) iodide (0.1 to 0.15 equivalents) was placed in the reaction vessel and flushed with argon for 30 minutes. The solution was added onto the copper salt via a syringe under inert conditions and the flask was closed after 10 minutes of bubbling with argon. Afterwards, the mixture was stirred for 48 h at room temperature. Subsequently, the solution was washed twice with aqueous ammonia solution (10%) and the polymer was precipitated into diethyl ether.

Results and Discussion

Controlled polymerization methods depend on the absence of side reactions like chain transfers or chain couplings. On the other hand, alkyne functionalities included in a monomer can cause such side reactions if radical polymerizations are used. To avoid

network formation or uncontrolled polymerization behavior, a protection of the alkyne group is necessary. Therefore, TMSPMA, where the triple bond is protected by trimethylsilyl, was chosen as monomer. The reversible addition-fragmentation chain-transfer polymerization (RAFT) is a very suitable polymerization technique with the advantage of no required metal catalyst. Even more, it is an appropriate method in particular for methacrylate based monomers.

To verify the control over a polymerization, kinetic studies have to be performed. A linear behavior of a plot of $\ln(M_t/M_0)$ over reaction time, whereas M_0 and M_t are the initial (M_0) and the actual (M_t) monomer concentration, indicates a pseudo first order kinetic. Thus, the concentration of radicals stays constant during the reaction and therefore the absence of termination reaction can be concluded. The linear increase of the molecular weight with increasing conversion and a PDI below 1.3 represents an additional strong indication for a polymerization mechanism that proceeds in a controlled way. As an example, the obtained results of a kinetic study of a copolymerization of TMSPMA and MMA are shown in Figure 1.

The linear appearance of both plots reveals a controlled behavior of the polymerization of TMSPMA. With this proof, the preparation of several different backbone-architectures is now possible. Accordingly, in addition to the homopolymer of TMSPMA, **P1**, random copolymers of TMSPMA and MMA with different ratios, **P2** and **P3**, as well as a block copolymer of TMSPMA and MMA, **P4**, were synthesized. In Table 1 selected properties of the obtained polymers are summarized, including composition and characteristic molecular data like the number average molecular weight (M_n) and the PDI.

Gel permeation chromatography (GPC) measurements revealed monomodal traces with PDI values lower than 1.3. The M_n and PDI values were calculated using a PMMA calibration. The determination of the general polymer composition was possible by measuring ^{1}H nuclear magnetic resonance (NMR) spectra. A molecular weight (M_n) determination by NMR measurement is possible by comparison of end group related signals with backbone specific signals. Due to the only theoretically complete functionalization of all polymeric chains with a CTA end group, the values obtained with these calculations are not very accurate. Nevertheless, most of the obtained molecular weight values are in the same range as the values obtained by GPC.

In addition to GPC and NMR spectroscopy, detailed analysis was performed with matrix assisted laser desorption/ionization

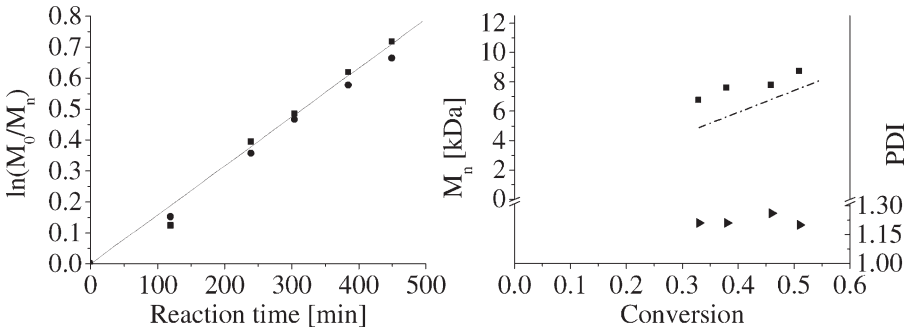


Figure 1.
Kinetics for the random copolymerization of TMSPMA and MMA (**P2**, $(P(TMSPMA)_{0.5}\text{-}r\text{-}(MMA)_{0.5})$. Left: semi-logarithmic kinetic plot (TMSPMA: ■, MMA: ●) and the linear fit (——) (M_0: initiating monomer concentration, M_t: monomer concentration at certain times). Right: number average molecular weight (M_n) (■) and PDI (▶) *versus* conversion ($CHCl_3$:triethylamine:isopropanol (94:2:4) as an eluent and calculated according to the PMMA standards used), theoretical molecular weight calculated from conversion (dotted line).

Table 1.
Selected properties of the synthesized protected and deprotected alkyne containing homo- and copolymers.

Polymer	Code	M_n[a)] (NMR) [Da]	M_n[a)] (GPC) [Da]	DP (NMR) TMSPMA/MMA	PDI[a)] (GPC)
P(TMSPMA)	**P1**	6,000	5,600	30	1.25
P(PMA)	**D1**		4,500		1.23
P(TMSPMA$_{0.5}$-*r*-MMA$_{0.5}$)	**P2**	8,300	8,600	28/28	1.23
P(PMA$_{0.5}$-*r*-MMA$_{0.5}$)	**D2**		8,900		1.14
P(TMSPMA$_{0.11}$-*r*-MMA$_{0.89}$)	**P3**	5,900	7,900	6/47	1.25
P(PMA$_{0.11}$-*r*-MMA$_{0.89}$)	**D3**		8,300		1.19
P(MMA$_{0.42}$-*b*-TMSPMA$_{0.58}$)[b)]	**P4**	13,500	9,400	50/35	1.25
P(MMA$_{0.42}$-*b*-PMA$_{0.58}$)	**D4**		9,800		1.18

[a)]Calculated using PMMA calibration.
[b)]PMMA ($M_n = 3{,}500$; PDI = 1.12) was used as a macro chain transfer agent for the block copolymerization.

time-of-flight mass spectrometry (MALDI-TOF MS).[28] The complete spectrum reveals a molecular weight distribution occurring much lower in average than expected according to NMR and GPC results. Nevertheless, it is possible to determine the exact molar mass of the expected chemical structures with this mass spectrometry technique (Figure 2).

The deviation in the calculated mass of the expected structures and the measured m/z values is less than 0.2 Da. The expected main-distribution (1 in Figure 2) appears smaller than the one corresponding to chain-transfer-side-reactions (3 in Figure 2). Distribution 2 in Figure 2 represents a polymer initiated by AIBN. However, MALDI-TOF MS does not allow any

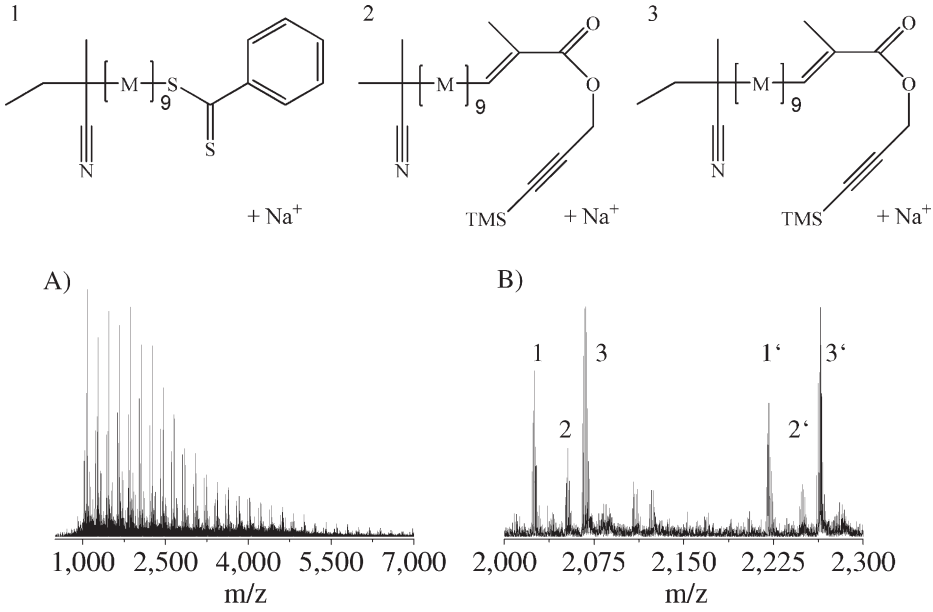


Figure 2.
MALDI-TOF/MS spectrum of **P1** (used matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), used salt: NaI). A) Spectrum in full range. B) Magnification of the m/z range from 2,000 to 2,300 (1′–3′ represent the corresponding structures with one additional repeating unit). Schematic representation of the proposed chemical structures (M represents the repeating unit of TMSPMA).

quantitative conclusions between different structures. It can be assumed that the CBDB-end group is partially cleaved off as a result of the MALDI-process itself, as already investigated in earlier studies of our group.[29] The two small distributions around 2125 Da in Figure 2 could not be assigned with less than 1 Da deviation(the most plausible structures are related to chain coupling reactions).

The deprotection of the alkyne functionalities in **P1**–**P4** provided the polymers **D1**–**D4** with the new repeating unit of propargyl methacrylate (PMA). The use of tetra-*n*-butylammonium fluoride trihydrate (TBAF × 3 H_2O) and acetic acid ensured the deprotection of the acetylene function without cleavage of the ester group. Quantitative deprotection could be easily validated by ^{1}H-NMR measurement that revealed in all cases the total absence of the specific signal of the protection group at 0.19 ppm after deprotection. The results from NMR and GPC measurement are shown for **D2** in Figure 3. No negative influences for PDI and M_n occurred. Furthermore, due to the application of several precipitation steps, the PDI was even lower after the deprotection than before.

The modification of **D1**, the deprotected homopolymer, with 10-(azidomethyl)anthracene in a CuAAC reaction provides a functional polymer bearing a fluorescent group. Moreover, the comparison of the UV-vis spectra revealed an absorbance appearing at 395 nm, which is specific for the anthracene group. A GPC measurement with a UV-detector using a wavelength of 395 nm further verified the functionalization of the polymer and ensured that not just a blend was prepared (Figure 4). Also in this case the CuAAC modification is mild enough to secure the narrow molecular weight distribution of the polymer.

Further characterization techniques such as NMR spectroscopy and MALDI-TOF/MS also indicated the presence of anthracene functionalities in the polymer. NMR spectroscopy allows the calculation of the degree of functionalization (DF). According to the measured signals and their integrals, the DF of **C1** is >95%. Although this value is limited by the NMR accuracy, it illustrates the effectiveness of the employed modification method. During analysis of the measured MALDI-TOF mass spectra (Figure 5), a problem related to the structure of the anthracene based substituent occurred. Due to its absorption behavior, which is close to the absorption of the used matrices like dithranol, the spectrum allowed no determination of M_n

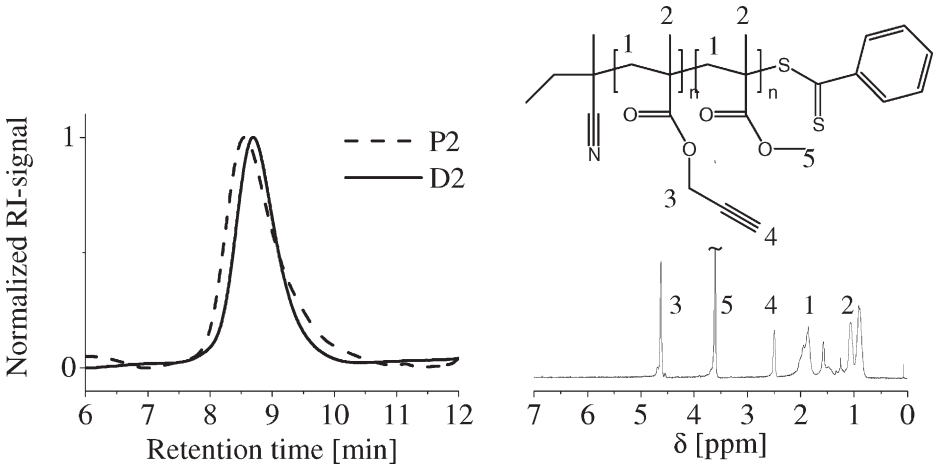


Figure 3.
Left: GPC trace of **P2** and **D2**. Right: ^{1}H-NMR spectrum of **D2** (250 MHz, $CDCl_3$).

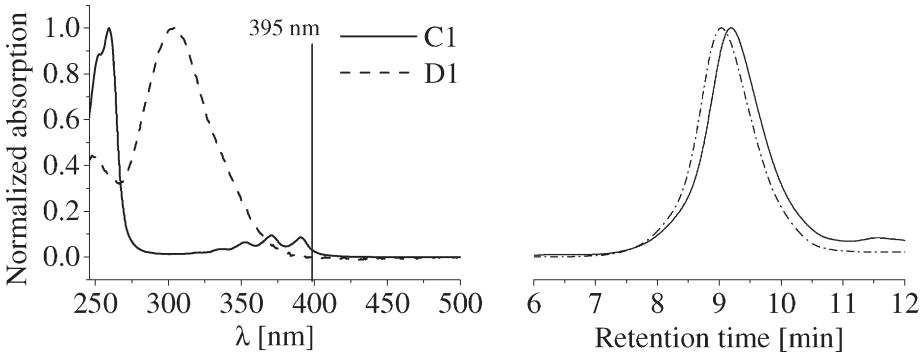


Figure 4.
Left: Comparison of the UV-vis detected GPC traces of **D1** and **C1** normalized according to their RI signals. Right: GPC traces of **C1** detected with RI- (––) and UV-vis detector (——) (UV-vis detector: 395 nm).

or the PDI value. Nevertheless, magnification of the spectrum revealed a new repeating unit mass of 357 Da. This represents the expected molecular weight of the synthesized functional monomeric unit.

The synthesis of well-defined glycopolymers is of great interest for biological applications such as biorecognition. Azide functionalized sugar units, *i.e.* $Glu(OAc)_4$-Et-N_3, are required to prepare such sugar containing polymers with the CuAAC reaction. The introduction of this functionality to **D3** ($M_n = 8300$; PDI = 1.19) led to a well-defined glycopolymer with a narrow molecular weight distribution ($M_n =$ 15,000; PDI = 1.13). The degree of functionalization (DF) is calculated to be $> 95\%$ according to the NMR measurement, which indicates that almost each alkyne function has successfully reacted with $Glu(OAc)_4$-Et-N_3. A comparison of the GPC traces of **D3** and **C2** showed a significant increase of the hydrodynamic volume due to the sugar substituents.

A wide range of properties can be reached by synthesis of grafted copolymers. To obtain this class of polymers, in principle three approaches are possible. The so-called ''grafting through'' method uses macromonomers, whereas the ''grafting from'' technique polymerizes the second chains from a backbone polymer that is able to initiate several sidechain polymerizations working as a macro initiator. Here, the ''grafting onto'' approach was used. The possible disadvantages of this method, an incomplete functionalization and reaction condition that are too rough for well-defined backbone polymers, can be

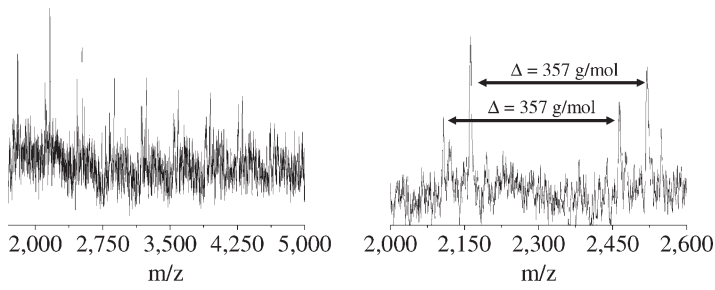


Figure 5.
Left: MALDI-TOF/MS-spectrum of **C1** (matrix: DCTB, salt: NaI). Right: Magnification of the m/z range from 2,000 to 5,000.

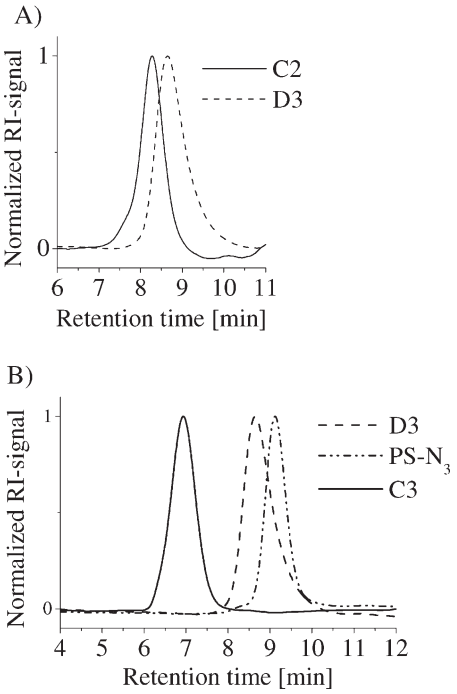


Figure 6.
A) Comparison of the GPC traces of **D3** and the glycopolymer **C2**; B) **D3**, PS-N_3 and the graft copolymer **C3**.

overcome by the use of suitable "click reactions" (in this case provided by the CuAAC reaction).

The synthesis of a graft copolymer using **D3** and PS-N_3 led to **C3**, P((PMA_6-*r*-MMA_{47})-*g*-PS_{72}). The purified polymer with a narrow molecular weight distribution was obtained after purification by preparative GPC. The determined values ($M_n = 52{,}700$ Da; PDI = 1.08; Figure 6, B), which were obtained by calculation against polystyrene standards, are close to the expected molecular weight of 52,000 Da. The DF was found to be 82% for **C3** according to the characterization by NMR spectroscopy.

Conclusion

In this study, various polymer architectures containing the protected alkyne containing methacrylate monomer, TMS-propargyl methacrylate (TMSPMA), were investigated in detail. The random and block copolymers of TMSPMA and MMA were synthesized by RAFT polymerization. The obtained universal backbone was characterized in detail by ^{1}H-NMR spectroscopy, GPC and MALDI-TOF mass spectrometry. The RAFT synthesis of the random and the block copolymers of TMSPMA and MMA are presented here for the first time. In addition, several functional groups such as sugar, polymer and optically active groups were introduced via the coppercatalyzed "click"-chemistry (a 1,3-dipolar cycloaddition) to the universal homopolymer and random copolymer backbones preserving their relatively low polydispersity indices (PDI < 1.3). Finally, we have obtained tailor-made macromolecules with various functionalities and narrow molecular weight distributions, which were characterized by GPC, ^{1}H NMR and UV-VIS spectroscopy as well as MALDI-TOF mass spectrometry techniques. In future studies, subsequent "click" reactions will be performed to obtain smart materials bearing multiple functional groups.

Acknowledgements: The authors wish to acknowledge the Dutch Polymer Institute (DPI), the Fond der chemischen Industrie (FCI) and the Thüringer Kultusministerium (grant no. B515-07008) for the financial support of this study.

[1] D. A. M. Egbe, E. Tekin, E. Birckner, A. Pivrikas, N. S. Sariciftci, U. S. Schubert, *Macromolecules* **2007**, *40*, 7786–7794.
[2] N. Adams, U. S. Schubert, *Adv. Drug Delivery Reviews* **2007**, *59*, 1504–1520.
[3] R. Langer, *Nature* **1998**, *392*, 5–10.
[4] E. S. Gil, S. M. Hudson, *Prog. Polym. Sci.* **2004**, *29*, 1173–1222.
[5] G. Coullerez, P. H. Seeberger, M. Textor, *Macromol. Biosci.* **2006**, *6*, 634–647.
[6] A. Marsh, A. Khan, D. M. Haddleton, M. J. Hannon, *Macromolecules* **1999**, *32*, 8725–8731.
[7] X. Chen, B. Gholamkhass, X. Han, G. Vamvounis, S. Holdcroft, *Macromol. Rapid Commun.* **2007**, *28*, 1792–1797.
[8] Y. Li, J. Yang, B. C. Benicewicz, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4300–4308.
[9] R. Luxenhofer, R. Jordan, *Macromolecules* **2006**, *39*, 3509–3516.

[10] J. M. Pollino, M. Weck, *Chem. Soc. Rev.* **2005**, *34*, 193–207.
[11] C. Ott, R. Hoogenboom, U. S. Schubert, *Chem. Commun.* **2008**, *30*, 3516–3518.
[12] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.
[13] H. C. Kolb, K. B. Sharpless, *Drug Discovery Today* **2003**, *8*, 1128–1137.
[14] M. Szwarc, *Nature* **1956**, *178*, 1168–1169.
[15] K. Matyjaszewski, A. H. E. Müller, *Prog. Polym. Sci.* **2006**, *31*, 1039–1040.
[16] W. A. Braunecker, K. Matyjaszewski, *Prog. Polym. Sci.* **2007**, *32*, 93–146.
[17] V. Coessens, T. Pintauer, K. Matyjaszewski, *Prog. Polym. Sci.* **2001**, *26*, 337–377.
[18] S. Perrier, P. Takolpuckdee, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5347–5393.
[19] D. Fournier, R. Hoogenboom, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 1369–1380.
[20] R. Hoogenboom, B. C. Moore, U. S. Schubert, *Chem. Commun.* **2006**, *38*, 4010–4012.
[21] C. Haensch, S. Hoeppener, U. S. Schubert, *Nanotechnology* **2008**, *19*, 035703/1–035703/7.
[22] V. Ladmiral, G. Mantovani, G. J. Clarkson, S. Cauet, J. L. Irwin, D. M. Haddleton, *J. Am. Chem. Soc.* **2006**, *128*, 4823–4830.
[23] M. W. M. Fijten, R. M. Paulus, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3831–3839.
[24] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559–5562.
[25] For examples, see *e.g.*: a) R. Hoogenboom, M. A. R. Meier, U. S. Schubert, *Macromol. Rapid Commun.* **2003**, *24*, 16–32 b) S. Schmatloch, M. A. R. Meier, U. S. Schubert, *Macromol. Rapid Commun.* **2003**, *24*, 33–46 c) H. Zhang, M. W. M. Fijten, R. Hoogenboom, R. Reinierkens, U. S. Schubert, *Macromol. Rapid Commun.* **2003**, *24*, 81–86 d) M. A. R. Meier, R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Commun.* **2004**, *25*, 21–33 e) H. Zhang, U. S. Schubert, *Macromol. Rapid Commun.* **2004**, *25*, 1225–1230 f) M. W. M. Fijten, M. A. R. Meier, R. Hoogenboom, U. S. Schubert, *J. Polym. Sci. : Part A: Polym. Chem.* **2004**, *42*, 5775–7583.
[26] E. F. V. Scriven, K. Turnbull, *Chem. Rev.* **1988**, *88*, 298.
[27] J. Xia, K. Matyjaszewski, *Macromolecules* **1997**, *30*, 7697–7700.
[28] For examples see, *e.g.*: M. A. R. Meier, U. S. Schubert, *Rapid Commun. Mass Spectrom.* **2003**, *17*, 713–716.
[29] M. W. M. Fijten, M. A. R. Meier, R. Hoogenboom, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5775–5783.

