Macromolecules

A Modular Route for the Synthesis of ABC Miktoarm Star Terpolymers via a New Alkyne-Substituted Diphenylethylene Derivative

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Supporting Information

ABSTRACT: We introduce a modular route for the synthesis of well-defined ABC miktoarm star terpolymers. To this aim, the synthesis of a 1,1-diphenylethylene derivative bearing a protected alkyne function (1-[(4-(tert-butyldimethylsilyl)-ethynyl)phenyl]-1-phenylethylene) was developed. This compound was for the first time employed in sequential anionic polymerization to readily prepare alkyne mid-functionalized diblock copolymers with polybutadiene as first and a poly(alkyl methacrylate) (poly(*tert*-butyl methacrylate), poly(*N*,*N*-dimethylaminoethyl methacrylate)) as second block. For the third



arm controlled radical polymerization methods (polystyrene, poly(*tert*-butyl methacrylate), poly(*N*,*N*-dimethylaminoethyl methacrylate)) and anionic ring-opening polymerization (poly(ethylene oxide)) were used to separately prepare homopolymers with an azido function. Afterward, azide—alkyne Huisgen cycloaddition was successfully employed to synthesize a library of ABC miktoarm star terpolymers with different molecular weights and chemical compositions via modular combination of the functionalized diblock copolymers and homopolymers. The resulting new ABC miktoarm star terpolymers showed narrow, monomodal molecular weight distributions with dispersities typically below 1.10, as determined by size exclusion chromatography.

■ INTRODUCTION

Polymer architecture and composition is a decisive factor for controlling structure formation both in bulk and in solution. Besides the choice of monomer and the number and sequence of polymeric building blocks the way of molecular conjunction of these blocks is of outermost importance. Compared to their linear analogues, miktoarm star terpolymers, where the polymer chains are connected at one common junction point,¹ present a much more complex system. A variety of unique bulk morphologies were found,²⁻⁴ which are inaccessible by linear triblock terpolymers. This is a direct consequence of the confined geometry of the polymer chains, which forces the common junction points of the three different blocks to be aligned in a 1-dimensional fashion. These miktoarm star terpolymer morphologies were also utilized for generating cylindrical, compartmentalized particles by selective crosslinking of one block.⁵ In addition, theoretical studies suggest that even more complex morphologies are expected under cylindrical confinement of ABC miktoarm star terpolymers.⁶ Depending on the length ratio of the respective arms, Hillmyer, Lodge, and co-workers^{7,8} obtained different multicompartment structures in aqueous solution from ABC miktoarm star terpolymers with a fluorinated segment. These ranged from hamburger micelles to segmented wormlike micelles and nanostructured vesicles.

The conjunction of three chains at one common linking point leads to special requirements concerning the synthetic

strategy. The main difficulties are (1) the exact functionalization of a diblock copolymer with a functional group or polymer block at the junction of the two blocks and (2) the stoichiometry of the linking reaction. Four different synthetic strategies have been reported so far for miktoarm star terpolymers.

One approach uses the different reactivity of living anionic polymer chains toward the chlorine-silicon groups of trichlorosilanes. Using methyltrichlorosilane as linking agent, Hadjichristidis and co-workers synthesized a miktoarm star terpolymer consisting of polyisoprene, polystyrene, and polybutadiene.⁹ However, the sequence of introduction of arms is strongly limited to the reactivity and steric demand of the polymeric anions, and adaption to other monomers requires a modification of the method.^{10,11} The second anionic approach utilizes macromonomers with nonhomopolymerizable end groups which were directly sequentially copolymerized with two sorts of monomers.^{2,12-14} In another approach, first diblock copolymers were synthesized carrying functional groups at the junction point of the two blocks. Again, nonhomopolymerizable compounds or special polymerization strategies have to be employed to ensure that only one functional group is located exactly in between the two

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Scheme 1. Synthetic Route for the Synthesis of ABC Miktoarm Star Terpolymers for the Example of a Star Consisting of Arms of Polybutadiene, Poly(*tert*-butyl methacrylate), and Polystyrene



polymeric building blocks. Up to now, mainly hydroxyl functions were used to conjugate the third block, which were introduced via a 1,1-diphenylethylene (DPE) derivative^{15,16} or 2-methoxymethyloxymethyloxirane¹⁷⁻¹⁹ as end-capping molecule. This hydroxyl function serves as anchoring point for the third block, which can be "grafted from" by anionic ring-opening polymerization (AROP)^{15–17} or controlled radical polymerization (CRP) after appropriate modification¹⁹ or "grafted to" via direct esterification.¹⁸ Hirao and co-workers recently used in-chain-benzyl bromide-functionalized diblock copolymers for the miktoarm star terpolymer synthesis involving specially designed anionic linking reactions.²⁰

The possibility of constructing complex polymeric architectures with controlled radical polymerization methods increased within the past decade.^{21,22} This supported the development of new strategies for the synthesis of ABC miktoarm star terpolymers where anionic polymerization is not involved. In addition, click reactions in general, or copper(I)-catalyzed azide—alkyne cycloaddition (CuAAC) in particular have become powerful tools for highly efficient linking of polymeric building blocks.^{23–25} These novel synthetic routes take advantage of the orthogonality of the different polymerization/ligation methods, which is a prerequisite for the synthesis of well-defined ABC miktoarm star terpolymers. By designing special core molecules with three different functionalities, the arms can be "grafted onto" or "grafted from" in different steps.^{26–31}

Herein, we present a more general method by combining anionic polymerization, employed for the synthesis of readily alkyne mid-functionalized diblock copolymers, with other polymerization techniques via azide—alkyne Huisgen cycloaddition (Scheme 1). Barner-Kowollik and co-workers already reported the ligation of alkyne mid-functionalized homopolymers with azide-bearing homopolymers.³² However, only A_2B miktoarm star terpolymers were accessible. The synthesis of an alkyne mid-functionalized diblock copolymer consisting of polystyrene and poly(*tert*-butyl acrylate) was also reported.^{33,34} Nevertheless, multiple polymer analogous reactions had to be conducted and/or switching the polymerization system was necessary. Thus, we synthesized 1-[(4-(*tert*butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene to directly prepare midchain alkyne-substituted diblock copolymers via sequential anionic polymerization. Because of the direct introduction of the alkyne group into the diblock copolymer by the use of DPE chemistry, a wide variety of functional diblock copolymers are accessible, and except for hydrolysis no tedious transformation reactions have to be conducted. The obtained diblock copolymers were afterward ligated with different azidebearing homopolymers prepared by atom transfer radical polymerization (ATRP), reversible addition–fragmentation chain transfer (RAFT) polymerization, and anionic ringopening polymerization via azide–alkyne click chemistry. Different novel ABC miktoarm star terpolymers were synthesized utilizing this modular combination.

EXPERIMENTAL SECTION

Materials. For the purification of monomers, reagents, and solvent and the synthesis of used compounds see the Supporting Information.

Synthesis of 1-[(4-(tert-Butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene (Click-DPE). The starting molecule 1-(4bromophenyl)-1-phenylethylene was synthesized as described elsewhere.³⁵ The synthetic protocol for the coupling reaction with the protected alkyne derivative was adopted from the literature.³⁶ First, 1-(4-bromophenyl)-1-phenylethylene was dissolved in piperidine (~50 mg/mL) and bis(triphenylphosphine)palladium(II) dichloride (0.03 equiv) and CuI (0.004 equiv) were added under a nitrogen atmosphere. After degassing with nitrogen for 30 min, tertbutyldimethylsilylacetylene (1.2 equiv) was added dropwise at 50 °C, and the solution was stirred overnight. The reaction mixture was filtered, the solvent was evaporated, and the crude product was dissolved in THF. After addition of water, the product was extracted with hexane for three times. The organic fractions were dried over sodium sulfate, and the solvent was evaporated to obtain a brown oil. This was further purified by column chromatography with hexane as solvent to obtain a clear oil. Distillation of the product was not possible even under high vacuum conditions. Before the use in anionic polymerization, the compound was freeze-dried from benzene solution on a high vacuum line and subsequently dissolved in dry THF to obtain a stock solution of low viscosity. sec-BuLi was added dropwise (typically 1-2 drops) under nitrogen flow until a deeply violet color was obtained. Besides proving the absence of impurities, the persistent

Table 1. Molecular	Characterization o	f Alkyne Mid-Function	nalized PB-b-P2VP,	PB-b-PtBMA, a	and PB-b-PDMAEM	A Diblock
Copolymers						

	sample ID ^a	<i>M</i> _n PB-precursor ^{<i>b</i>} [kg/mol]	$N(PB)^b$	N(2nd block) ^c	$M_{\rm n} \ { m diblock}^d \ [m kg/mol]$	\mathcal{D} diblock ^e	f_{alkyne}^{f}
cBV1	$(cB_{40}V_{58}^{14.7})$	5.9	109	81	14.7	1.02	1.16
cBV2	$(cB_{22}V_{76}^{14.0})$	3.1	58	101	14.0	1.03	1.20
cBV3	$(cB_{70}V_{28}^{17.2})$	12.0	223	46	17.2	1.02	n.d.
cBT1	$(cB_{76}T_{22}^{17.1})$	13.0	242	27	17.1	1.03	0.93
cBT2	$(cB_{49}T_{49}^{12.3})$	6.0	111	42	12.3	1.03	n.d.
cBD	$(cB_{58}D_{40}^{17.0})$	9.8	181	44	17.0	1.06	n.d.

^aThe subscripts denote the molecular weight fraction and the superscript the overall molecular weight including the click-DPE unit. ^bDetermined by MALDI-ToF MS. ^cCalculated by ¹H NMR or in the case of PtBMA as second block by the difference in the MALDI-ToF MS spectra of diblock and precursor. ^dThe overall molecular weight was determined by a combination of MALDI-ToF MS and ¹H NMR in the case of cBV's and cBD and by MALDI-ToF MS in the case of cBT's. The molecular weight of the diblock includes the DPE unit. ^eMeasured from THF-SEC calibrated with polystyrene standards; in the case of cBD salt-THF-SEC was used. ^fThe degree of alkyne functionalization f_{alkyne} was determined by UV–vis measurements of the perylene-modified diblock copolymers.

color also served as indication for the purity of the stock solution. ¹H NMR (300 MHz, CDCl₃): δ = 7.50–7.27 (m, 9H, Ar), 5.50 (s, 2H, C=CH₂), 1.03 (s, 9H, SiC(CH₃)₃), 0.22 (s, 6H, SiCH₃).

Polymerizations. Sequential Living Anionic Polymerization in THF. All polymerizations were carried out at low temperatures in a thermostated laboratory autoclave (Büchi) under dry nitrogen atmosphere using THF as solvent. The day before polymerization, freshly distilled THF (~250 mL for 15 g of polymer) was treated with 1 mL of sec-BuLi per 100 mL of solvent at -20 °C, followed by stirring overnight to form lithium alkoxides. These exhibit stabilizing effects on the living chain end of polybutadiene and furthermore in the case of methacrylate-type monomers no addition of LiCl is necessary to obtain well-defined polymers.³⁷ For the diblock copolymers, first butadiene was initiated with sec-BuLi at -70 °C and then polymerized at -50 to -15 °C depending on the block length of the different polymerizations. To ensure complete consumption of the butadiene the polymerization was followed by in-line NIR fiber-optic spectroscopy. The living polybutadienyl anion was end-capped with 1-[(4-(tert-butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene (1.1-1.5 equiv) at -50 °C for 2 h. Before and after the addition of the click-DPE samples for SEC and MALDI-ToF MS were withdrawn. In the case of poly(2-vinylpyridine) (P2VP) as second block the monomer was added at -70 °C and polymerized for 5 min. After termination with degassed methanol the polymer (cBV) was isolated by precipitation in water. For the diblock copolymers with tert-butyl methacrylate (tBMA) the monomer addition was conducted at -70 $^{\circ}$ C, and the polymerization took place at -45 $^{\circ}$ C for 1 h before it was terminated with degassed methanol. After the addition of the tBMA the violet color of the DPE end-capped living anion slowly faded away. The final polymer (cBT) was precipitated in a mixture of isopropanol/ water 3/1 (v/v). For the third type of diblock the N,Ndimethylaminoethyl methacrylate (DMAEMA) was injected into the reactor at -70 °C and polymerized for 1 h. Immediately after addition of the monomer the color of the DPE end-capped polybutadienyl anion vanished completely. After termination with degassed methanol, the resulting polymer (cBD) was dialyzed against THF and finally freeze-dried from dioxane. The molecular weights of the diblock copolymers with P2VP or PDMAEMA as second block were calculated by a combination of MALD-ToF MS and ¹H NMR. Therefore, the M_n of the polybutadiene (PB) precursor polymer was determined by mass spectrometry. By the relative molar ratios of the characteristic signals of PB (5.10-5.60 ppm, 2H 1,2-PB; 5.70-5.15 ppm, 1H 1,2-PB and 2H 1,4-PB) and P2VP (8.50-8.00 ppm, 1H) or PDMAEMA (4.30-3.90 ppm, 2H) the overall molecular weight was calculated using the PB precursor molecular weight as reference. The $M_{\rm p}$ of the PB-*b*-P*t*BMA diblock copolymers was directly measured by MALDI-ToF MS. All the data for the diblock characterization are summarized in Table 1.

Alkyne Deprotection. For the deprotection procedure, the respective polymer was dissolved in THF (~0.1 g/mL) and degassed for 30 min. Then, 10 equiv of tetrabutylammonium fluoride (1 M solution in THF) relative to alkyne functions were added at 0 $^{\circ}$ C and

stirred at this temperature for 2 h. After warming up to room temperature the solution was stirred overnight. The polymer was precipitated in pure water or isopropanol/water 3/1 (v/v) for PB-b-P2VP and PB-b-PtBMA, respectively. Afterward, the polymer was dissolved in THF and dialyzed against THF (MWCO 1000 g/mol) to remove impurities. Finally, the polymers were freeze-dried from dioxane. In the case of the diblock copolymer with DMAEMA the reaction mixture was directly dialyzed against THF prior to freeze-drying.

Click Reactions. For the determination of the degree of functionalization with alkyne-substituted DPE, test click reactions with N-(1-heptyloctyl)-N'-(hexyl-6'-azido)-perylene-3,4,9,10-tetracaboxylic acid bisimide were conducted. In a typical run, 100 mg of the deprotected diblock copolymer was dissolved in 5 mL of THF in a screw-cap glass. Then, 2 equiv of the azido-functionalized perylene bisimide relative to the alkyne function was added. After purging with nitrogen for 10 min, 1 equiv of CuBr was added, followed by further degassing for 10 min. By addition of 1 equiv of N,N,N',N',N"pentamethyldiethylenetriamine (PMDETA) as ligand, the click reaction was started and stirred at room temperature for 3 days. After termination by exposure to air, the remaining copper was removed by filtration over a short silica gel column. Preparative SEC with THF as eluent was employed to remove excess perylene. An intense red-colored polymer was obtained after freeze-drying from dioxane.

The click reactions for the construction of the miktoarm star terpolymers were conducted in a similar manner. Typically, the molar ratios of alkyne function:azido function:CuBr:PMDETA was set to 1:1:1:1 (if not stated elsewhere), and the polymer concentration was \sim 20 mg/mL in THF. The reactions were conducted at room temperature and followed by withdrawing samples for SEC measurements. Finally, when no further changes in the SEC eluogramms were observed, the resulting miktoarm star terpolymer was purified by passing through a small silica gel column to remove copper. The polymers were obtained as white powders after freeze-drying from dioxane.

RESULTS AND DISCUSSION

Synthesis of 1-[(4-(*tert***-Butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene (Click-DPE).** The key compound of this modular route toward ABC miktoarm star terpolymers (Scheme 1) was directly synthesized by the palladium-catalyzed Sonogashira coupling reaction between 1-(4-bromophenyl)-1phenylethylene and *tert*-butyldimethylsilyl protected acetylene. Similar compounds, like 4-(trimethylsilyl)ethynylstyrene³⁶ and methacrylate derivatives as 3-trimethylsilyl-2-propynyl methacrylate,³⁸ have already been synthesized and used in anionic polymerization to obtain polymers with predictable molecular weights and narrow distributions. As known for DPE and its derivatives homopolymerization of such compounds is not possible due to steric hindrance.³⁹ In contrast to methods reported in the literature,^{33,34} this synthetic advantage enables us to use one sequential polymerization process to selectively incorporate exactly one alkyne function between the two polymeric blocks under adequate choice of monomers. The click-DPE was purified via column chromatography to give a clear viscous oil. The chemical structure and the purity were confirmed by ¹H NMR spectroscopy (Figure 1a).



Figure 1. ¹H NMR spectra of (a) 1-[(4-(*tert*-butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene (click-DPE), (b) the protected alkyne-functionalized diblock cBT2, and (c) the corresponding diblock after hydrolysis of the silyl-protecting group (solvent signals are striked out).



Figure 2. UV–vis absorption spectrum of the adduct of 1,1diphenylethylene (dotted line) and 1-[(4-(*tert*-butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene (solid line) with *sec*-BuLi in THF. The inset shows the picture of the cuvette containing the living anion of the unsubstituted DPE (top) and the click-DPE (bottom).

The UV-vis spectrum of the deeply violet solution of the living anion (Figure 2) generated by reaction of 1-[(4-(*tert*-butyldimethylsilyl)ethynyl)phenyl]-1-phenylethylene with *sec*-BuLi shows a maximum at 549 nm. In contrast, the living anion of unsubstituted 1,1-diphenylethylene has a deep red color, and we determined the absorption maximum at around 500 nm under the same conditions.⁴⁰ This clear bathocromic shift originates from the conjugation of the π -system with the protected alkyne group. Similarly, Tsuda et al. reported a brownish-red color in the anionic polymerization of 4-(trimthylsilyl)ethylenstyrene,³⁶ in contrast to the orange color of polystyryl anions.⁴¹

Synthesis of Alkyne Midfunctionalized Diblock Copolymers. Butadiene was chosen for the first block and for the second block 2-vinylpyridine (2VP) or methacrylate type monomers as tert-butyl methacrylate (tBMA) and N,Ndimethylaminoethyl methacrylate (DMAEMA). The anionic polymerization of butadiene was conducted in THF at -50 to -15 °C (depending on the respective block length) using sec-BuLi as initiator. After complete conversion-as followed in situ with fiber-optics NIR spectroscopy-1.1 to 1.5 equiv of the click-DPE stock solution was added via syringe at -50 °C. The addition of the diphenylethylene derivative was clearly visible by the immediate change in color from a slight yellow to intensive dark violet. To ensure complete end-capping of the polybutadienyl anions, the solution was stirred at -50 °C for another 2 h. During this period, no fading or change in color was detected. Samples of the polybutadiene (PB) precursors for SEC analysis were withdrawn before and after addition of the click-DPE, respectively. As the pristine polybutadiene carries no chromophore, no UV signal was detected at 260 nm. After reaction with the click-DPE, a significant UV signal was detected, coinciding with the RI trace. No change in the shape of the peak was detectable, indicating the absence of unwanted side reactions. Furthermore, a small shift of the whole peak toward lower elution volumes took place (Figure S1). The molecular weight of the polybutadiene precursor was 5910 g/ mol before and 6270 g/mol after the addition of the click-DPE, as determined by MALDI-ToF MS (Figure S2). This is in good accordance with the expected increase of 320 g/mol for a click-DPE monoaddition.

With this new alkyne substituted DPE derivative we prepared three different types of midchain alkyne-functionalized diblock copolymers with narrow molecular weight distributions. In the case of 2-vinylpyridine as second block, the monomer was added at -70 °C and the polymerization was quenched after 5 min by the addition of degassed methanol. The overall composition and number-average molecular weight of the three different diblock copolymers (cBV1, cBV2, and cBV3) were determined by a combination of MALDI-ToF MS and ¹H NMR. The characterization of the synthesized diblock copolymers is given in detail in Table 1.

In addition, we also prepared different diblock copolymers with PtBMA (cBT1 and cBT2) or PDMAEMA (cBD) as the second block. The polymerization conditions for polybutadiene and the end-capping reaction were similar to the diblock copolymers consisting of butadiene and 2-vinylpyridine (cBV's). The *t*BMA polymerization was started at -70 °C. As the violet color of the anionic click-DPE chain end did not disappear the temperature was stepwise raised to -45 °C where the color slowly faded away. This indicated the start of the polymerization. In the case of cBD the monomer was also added at -70 °C; however, the color of the end-capped polybutadienyl anion disappeared immediately after the addition of the monomer. DMAEMA polymerized faster and already at -70 °C, as it shows a higher reactivity than *t*BMA. Similar to tBMA no change from colorless to violet was observed after complete consumption of the monomer. This substantiates the hypothesis that the click-DPE is only inserted after the polybutadiene block and not within or at the end of the methacrylate block. All data for the polybutadiene precursors and the final diblock copolymers are listed in Table 1.

Theoretically, in combination with *sec*-BuLi, our click-DPE can be used to initiate methacrylates for the generation of α -alkyne-functionalized homopolymers or block copolymers. In addition ω -alkyne-terminated homo- or block copolymers of nucleophilic monomers like styrene, butadiene, and their

Chart 1. Azido-Functionalized Homopolymers Synthesized via Different Polymerization Methods



derivatives can be prepared by end-capping with this alkynesubstituted DPE. The alkyne function is directly introduced into the polymers via DPE-chemistry. Except hydrolysis, no further polymer-analogous reaction steps are therefore necessary.

Hydrolysis of the Alkyne Mid-Functionalized Diblock Copolymers. The tetra-*n*-butylamonium fluoride-mediated hydrolysis of the protecting group was monitored via ¹H NMR by the disappearance of the characteristic methyl signals of the silyl group at 1.03 and 0.22 ppm. The signal at 1.03 is overlapping with the backbone signals of polybutadiene, whereas the signal at 0.22 is well separated from other signals. Therefore, for the latter signal the complete disappearance indicates the quantitative deprotection (Figure 1b,c).

As the molecular weights of the diblock copolymers exceeded 10 000 g/mol, the direct determination of the degree of alkyne substitution from the characteristic signals of the protecting group was too imprecise. Thus, to determine the degree of alkyne functionalization, a modification of the diblock copolymers with an azido-functionalized perylene bisimide⁴² was conducted via click chemistry at the example of cBV1, cBV2, and cBT1. After deprotection of the alkyne function and subsequent click reaction with 2 equiv of N-(1-heptyloctyl)-N'-(hexyl-6'-azido)perylene-3,4,9,10-tetracarboxylic acid bisimide (N₃-PBI), functionalization of the diblock copolymer was proven qualitatively by SEC measurements at a wavelength of 458 nm. The nonlabeled diblock copolymers did not show any significant UV activity at this wavelength, whereas perylene is UV-active. After complete removal of excess perylene by preparative SEC (as confirmed by SEC measurements at 458 nm), UV spectra were recorded in dichloromethane at a polymer concentration of 10^{-5} mol/L. Thus, by measuring the optical density and comparing the value of UV absorption at the maximum of the spectra ($\lambda = 525$ nm) with a pure N₃-PBI solution with $c = 10^{-5}$ mol/L, the degree of alkynefunctionalization was determined to be ~116% for cBV1 (see Figure S3A and Table 1). There might be some minor sources of error by weighing and by determination of the numberaverage molecular weight of the polymer by a combination of MALDI-ToF MS and ¹H NMR. Nevertheless, this value gives rise to the assumption that there might be incorporation of more than one click-DPE in the block copolymer even under the applied conditions. Multiple incorporation of the DPE derivative in the polybutadiene block can be excluded, as complete consumption of the monomer was guaranteed by in situ NIR spectroscopy. Similar results were obtained for the N₃-PBI-labeled cBV2, where also functionalization with more than one click-DPE took place (concluded from the determined degree of functionalization of 120%). Test reactions showed that living 2VP anions can attack click-DPE after extended reaction times (a more detailed description and the corresponding MALDI-ToF MS spectra can be found in the

Supporting Information). Here, one has to note that for the test reaction the conditions were dissimilar to the diblock synthesis as a 2-fold excess of click-DPE was used, and the reaction mixture was stirred for an additional hour after addition of the click-DPE. In contrast to this, for the synthesis of the diblock copolymers the excess of click-DPE was already present during the course of polymerization. Nevertheless, we suppose that the click-DPE is incorporated after complete consumption of the 2VP monomer. As can be seen from the determined degree of alkyne-functionalization for the cBV's the values of 116-120% were lower than the maximal value of 150% deduced from the use of 1.5 equiv of click-DPE regarding initiator. Consequently, even though the P2VP polymerization was terminated immediately after consumption of all monomer, to a small extent diblock copolymers were obtained, which partially might bear an additional click-DPE unit in, or more probably, at the end of the P2VP block.

Since methacrylates are generally not capable of adding diphenylethylene, incorporation of only one click-DPE unit at the block junction is expected for the diblcock copoylmers with butadiene as first and a methacrylate as second block.^{39,43} This is supported by the determined degree of alkyne-functionalization of 93% for the perylene modified cBT1 (Figure S3B). Taking into account the errors of weighing and determination of the number-average molecular weight, this can be assumed to be quantitative. Therefore, well-defined diblock copolymers bearing exactly one alkyne function in between the two blocks can be synthesized with our approach, if the second block is a methacrylate. Generally, also well-defined alkyne mid-functionalized diblock copolymers consisting of poly(2-vinylpyridine) as first block and a methacrylate type monomer as second block are accessible utilizing click-DPE.

Synthesis of ω -Azido Homopolymers. In principle, every homopolymer bearing an azido function can be clicked to the synthesized alkyne mid-functionlized diblock copolymers. Different polymerization methods are capable of generating azido-functionalized polymers in situ^{44,45} or by appropriate termination reactions⁴⁶ or postfunctionalization methods.⁴⁷ To demonstrate the broad applicability and modular strategy of our approach, we synthesized azidofunctionalized homopolymers utilizing three different polymerizations methods (Chart 1, for details of the corresponding synthetic procedure see the Experimental Section in the Supporting Information). Azido-functionalized polystyrene (PS-N₃) as model compound was synthesized via ATRP and subsequent transformation of the bromine end group with sodium azide.⁴⁷ By using an azido-functionalized initiator, poly(*tert*-butyl methacrylate) was directly synthesized via ATRP.⁴⁵ This can be hydrolyzed to yield poly(acrylic acid). Similarly poly(N,N-dimethylaminoethyl methacrylate) as functional stimuli-responsive polymer was polymerized via RAFT employing an azido-functionalized chain transfer agent

(CTA).⁴⁴ Poly(ethylene oxide) (PEO) was achieved via anionic ring-opening polymerization (AROP) and can serve as watersoluble block. Therefore, we utilized the possibility of quenching living polymer anions with azido acid chlorides⁴⁶ to obtain azido-terminated PEO. In all cases the presence of an azido function was proven by IR measurements and additionally with MALDI-ToF MS or ¹H NMR except for *Pt*BMA-N₃ (see characterization of ω -azido homopolymers in the Supporting Information). The advantage of the applied "grafting-onto" method is that the third arm is polymerized and characterized separately. The molecular characterizations of the different polymers are summarized in Table 2.

Table 2. Molecular Characterization of Azido-Functional Homopolymers

sample ID	$M_{\rm n}$ [kg/mol]	Đ
PS1-N3 ^a	3.7	1.07
PS2-N3 ^a	5.9	1.10
PS3-N3 ^a	8.3	1.06
PEO-N3 ^b	6.6	1.02
PtBMA-N3 ^c	7.6	1.17
PDMAEMA-N3 ^d	5.4	1.20

^{*a*}Molecular weights and dispersities were determined by THF SEC using polystyrene standards. ^{*b*}Molecular weights and dispersities were determined by THF SEC using poly(ethylene oxide) standards. ^{*c*}Molecular weights and dispersities were determined by THF SEC using poly(*tert*-butyl methacrylate) standards. ^{*d*}MALDI-ToF MS was employed for determination of molecular weight and dispersity.

Synthesis of Miktoarm Star Terpolymers via Click Chemistry. Copper-catalyzed alkyne–azide cycloaddition (CuAAC) was utilized for the modular synthesis of ABC miktoarm star terpolymers via combination of alkyne midfunctionalized diblock copolymers with ω -azido-functionalized homopolymers of different length and monomer structure (Chart 1). Here, only the alkyne mid-functionalized diblock copolymers with a methacrylate as second block (cBT's and cBD) were used, as for 2-vinylpyridine partial incorporation of the click-DPE in or most probably at the end of the P2VP block could not be excluded completely.

Click Reactions with ω -Azido-Functionalized Polystyrene. To demonstrate the feasibility of this approach, we first conducted click reactions of the alkyne-functionalized diblock copolymers with different azido-functionalized PS homopolymers. One prerequisite of our approach is the 100% efficiency of the click reaction step, so that no laborious purification steps are needed when the educts are added in equimolar amounts.⁴⁸ Even though in literature linear and welldefined star shaped polymers with molecular weights close to 100 000 g/mol were produced via CuAAC, 49,50 we suppose that in our case the alkyne function at the block junction is sterically less amenable than an alkyne function in α - or ω -position. Our first trials with higher molecular weight polymers (exceeding 40 000–50 000 g/mol for the individual compounds) were not successful. Therefore, we chose moderate molecular weights of the individual compounds, so that the overall molecular weight did not exceed 25 000 g/mol and the functional groups were not too diluted. The course of the click reactions with cBT diblock copolymers was followed by SEC. The reactions were conducted under equimolar conditions. After 24 h the molecular weight distribution of the diblock copolymers cBT1 and cBT2 shifted completely (see Figure 3 and Figure

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Figure 3. THF-SEC (RI signal) of alkyne-functionalized diblock cBT1, azido-functionalized PS (PS1-N₃, PS2-N₃), and the corresponding ABC miktoarm star terpolymers (μ -BT1S1 and μ -BT1S2) obtained after equimolar click reaction for 24 h.

S4), resembling the successful generation of the desired miktoarm star terpolymers. However, despite equimolar reaction conditions in both cases there was still a minor amount of unreacted homopolymer left. Further SEC measurements showed that the peak of the PS1-N₃ already disappeared nearly completely after 11.5 h (Figure S5) for the click reaction with cBT2. Increasing the reaction time did not lead to any change in the eluogramm. Therefore, we additionally carried out a reaction between cBT1 and only 0.8 equiv of PS1-N₃. Under the same reaction conditions, again, a comparable amount of homopolymer was left (results not shown). We assume that during polymerization and work-up of the homopolymer, a minor part of the bromine group is eliminated, as already reported in the literature.⁵¹ This leads to a small amount of non-azido-functionalized homopolymer which cannot take part in the click reaction (see discussion of MALDI-TOF spectrum in the Supporting Information). This was also confirmed by the click reaction of cBT2 with PS3-N₃ (Figure S6). Under equimolar reaction conditions no further ligation took place after 15 h, leading to a non-negligible amount of unreacted diblock and homopolymer. In contrast to the click reactions with lower molecular weight polystyrenes the conversion of the click reaction with PS3-N₃ was much lower after 3.25 h (where the reaction was more or less finished in the other cases). Further addition of 0.5 equiv of homopolymer resulted in a complete shift of the diblock due to complete click efficiency as depicted in Figure S6. Thus, the degree of unfunctionalized polystyrene increased with increasing molecular weight.

Nevertheless, complete shifts of the molecular weight distributions of the miktoarm star terpolymers toward lower elution volumes compared to the pristine diblock copolymers were detected in all cases. This demonstrates the successful formation of ABC miktoarm star terpolymers. Additionally, the overall shifts of the resulting ABC miktoarm star terpolymers were not too distinct. This is in accordance with theory, where the hydrodynamic radius of star polymers is expected to be smaller than the hydrodynamic radius of a linear polymer with the same composition and molecular weight due to the higher segmental density of star polymers.⁵² All synthesized μ -BTS star terpolymers exhibited symmetrical peaks with a narrow molecular weight distribution. The theoretical molecular weights of

S	ample ID ^a	$DP(PB)^{b}$	DP(2nd block) ^c	$DP(3rd block)^d$	$M_{\rm n,th}^{e} [\rm kg/mol]$	$M_{n,app}^{f}$ [kg/mol]	D^{f}
μ -BT1S1	$(\mu - B_{63}T_{18}S_{18}^{20.7})$	242	27	36	20.7	28.0	1.03
μ -BT1S2	$(\mu - B_{57}T_{17}S_{26}^{22.9})$	242	27	57	22.9	30.0	1.03
μ -BT1E	$(\mu - B_{55}T_{16}E_{28}^{23.6})$	242	27	150	23.6	32.7	1.04
μ -BT1D	$(\mu - B_{58}T_{17}D_{24}^{22.4})$	242	27	34	22.4	31.5	1.10
μ -BT2S1	$(\mu - B_{38} T_{38} S_{23}^{15.9})$	111	42	36	15.9	20.5	1.03
μ -BT2S2	$(\mu - B_{33} T_{33} S_{33}^{18.1})$	111	42	57	18.1	22.4	1.03
μ -BT2S3 ^g	$(\mu - B_{29}T_{29}S_{40}^{20.5})$	111	42	80	20.5	25.0	1.03
μ -BT2E	$(\mu - B_{32} T_{32} E_{35}^{18.8})$	111	42	150	18.8	25.4	1.03
μ -BT2D	$(\mu - B3_4 T_{34} D_{31}^{17.6})$	111	42	34	17.6	20.8	1.11
μ -BDT ^g	$(\mu - B_{40}D_{28}T_{31}^{24.5})$	181	44	53	24.5	26.3	1.08
μ -BDE ^g	$(\mu - B_{42}D_{29}E_{28}^{23.5})$	181	44	150	23.5	32.5	1.06

Table 3. Molecular Characterization of ABC Miktoarm Star Terpolymers Obtained from Click Reactions with Alkyne Mid-Functionalized Diblock Copolymers

^{*a*}The number-average molecular weight of the ABC miktoarm star terpolymer was calculated from the respective values of diblock copolymers and the homopolymers. Therefore, the superscript denotes the theoretical number-average molecular weight of the ABC miktoarm star terpolymer and the indices the theoretical weight fraction of the respective blocks. ^{*b*}Degree of polymerization (DP) determined from MALDI-ToF MS of the PB-precursor. ^{*c*}Calculated by the difference in M_n determined by the MALDI-ToF MS spectra of diblock and precursor. ^{*d*}Calculated from the molecular weight of the 3rd block. ^{*e*}Theoretical molecular weight. ^{*f*}Apparent molecular weight and dispersity determined by SEC with polystyrene calibration. For the miktoarm star terpolymers containing PDMAEMA THF-SEC with additional 0.25 wt % tetrabutylammonium bromide (TBAB) was used. ^{*g*}In these cases the apparent molecular weight and dispersity were determined excluding the separated homopolymer peak.



Figure 4. THF-SEC (A) of alkyne-functionalized diblock copolymers cBT1, cBT2, the azido-functionalized PEO-N₃, and the corresponding ABC miktoarm star terpolymers (μ -BT1E and μ -BT2E) obtained after azide–alkyne click coupling and salt-THF-SEC traces (B) of cBD, PEO-N₃, and the resulting ABC miktoarm star terpolymer (μ -BDE) after dialysis. In all cases the RI signals are shown.

the ligated diblock copolymers. These are shown together with the apparent molecular weights and the respective dispersities in Table 3. Furthermore, an exemplarily ¹H NMR of μ -BT1S1 is shown in Figure S7. All characteristic signals of the polymeric building blocks are present in the obtained miktoarm star terpolymer.

Click Reactions with ω -Azido-Functionalized Poly-(ethylene oxide). These first successful test reactions with azido-functionalized polystyrene prove the feasibility of our approach. To prepare amphiphilic miktoarm star terpolymers, we conducted click reactions with PEO-N₃. First attempts under equimolar reaction conditions led to a non-negligible amount of unreacted diblock copolymer. Therefore, the click reactions were carried out with an excess of the functionalized PEO-N₃. By stepwise addition of PEO-N₃ to the reaction mixture, the equivalents necessary for a complete click reaction were determined (Figure S8). Therefore, in a first step, the reaction with 1 equiv of PEO-N3 was followed by SEC. As after 24 h no further change in the eluogram was detected, and still a significant amount of unreacted diblock copolymer was left over, 0.5 equiv of PEO-N₃ was added subsequently. Finally, after 3.5 h reaction time, a further 0.2 equiv of PEO-N₃ was

added to the click reaction containing already 1.5 equiv. As this did not result in a change compared to the eluogram after reaction with 1.5 equiv of PEO-N₃, the equivalents necessary for complete ligation were determined to be 1.5 equiv.

The reason for the use of such a huge excess of PEO-N₃ still remains unclear. From the amount of coupled product (~6 wt % from SEC) only a slight excess of the azido-functionalized compound would be reasonable. However, maybe partial elimination of the azido group of PEO or uncomplete functionalization due to side reaction during the end-capping reaction could be a feasible explanation (see discussion of MALDI-ToF spectrum in the Supporting Information). The respective SEC traces for the click reactions with cBT1, cBT2, and cBD (where the ratio of cBX:PEO-N₃ was minimum 1:1.5) are shown in Figure 4. In case of the diblock copolymers with PtBMA as second block the excess PEO-N₃ was easily removed during purification from copper with a short column of silica due to interactions with the column. Using PEO-N₃ in excess and subsequent removal of unreacted homopolymer guaranteed the complete conversion of the alkyne function.

However, in the case of the diblock cBD containing DMAEMA a higher amount of PEO homopolymer was left



Figure 5. Salt-THF-SEC (RI signal) of μ -BTD miktoarm star terpolymers obtained by click coupling of the alkyne-functionalized diblock copolymers (A) cBT1 and (B) cBT2 with the azido-functionalized PDMAEMA-N₃. As in both cases 2 equiv of PDMAEMA was used within the click reaction, SEC traces of the raw product and the miktoarm star terpolymer after dialysis are shown.

over after work-up. Further purification with a column, crystallization from cold THF, or dialysis in aqueous media did not reduce the amount of the undesired PEO homopolymer. A possible explanation could be that PEO forms hydrogen bonds with PDMAEMA, which therefore prevent the complete removal of excess PEO homopolymer. Here, one has to notice that for further applications, where the PEO serves as corona in aqueous solutions, this minor amount of PEO homopolymer is not problematic.

In contrast to the previous click reactions, distinct shifts of the molecular weight distributions of the ABC miktoarm star terpolymers compared to the corresponding diblock precursors were detected. The absence of a peak from residual diblock also gives evidence that all diblock copolymer chains carry an alkyne function. Like for the click reactions with $PS-N_3$ low dispersities of the resulting ABC miktoarm star terpolymers were detected (Table 3).

Click Reactions with ω -Azido-Functionalized Polv(N.Ndimethylaminoethyl methacrylate). To obtain PDMAEMA as a water-soluble polymer, which responds to both pH and temperature,⁵³ we used an azido-substituted CTA.⁴⁴ As the general applicability of our approach under equimolar conditions was proven we conducted the click reactions with a 2-fold excess of PDMAEMA-N₃ for 5 days, without optimizing the reaction time. With this reaction pathway we were also able to guarantee 100% conversion of the alkyne compound. The SEC traces of the raw product of the click reactions of the azido-functionalized PDMAEMA-N3 with the two cBT diblock copolymers are shown in Figures 5A and 5B, respectively. In both cases the molecular weight distributions of the miktoarm star terpolymers shifted completely in the corresponding SEC traces compared to their diblock copolymer precursors. The excess PDMAEMA-N3 was removed by dialysis in a mixture of methanol/isopropanol (2/1 v/v), where the miktoarm star terpolymer forms micelles with a polybutadiene core. Therefore, a dialysis membrane with a cutoff (50 000 g/ mol) much higher than the molecular weight of the homopolymer was used. The SEC traces of the obtained miktoarm star terpolymers are plotted in Figure 5A and B. In the case of μ -BT1D the tiny coupling shoulder at lower elution volume became more pronounced after dialysis. Therefore, we assume that this shoulder might be the result of some aggregation effects, which occurred for this reaction. Another explanation could be the oxidation of the amine, which leads to

the formation of amine oxide. For the dialysis of μ -BT2D even under extensive exchange of the solvent, the small residual peak from unreacted PDMAEMA-N₃ could not be removed completely. However, compared to the product peak this peak is negligible. The molecular characterization of the μ -BTD miktoarm star terpolymers is listed in Table 3. In a similar way a μ -BDT miktoarm star terpolymer consisting of the same monomer units was synthesized by ligation of cBD with PtBMA-N₃ (see Supporting Information and Table 3).

CONCLUSIONS

This general modular route for the synthesis of ABC miktoarm star terpolymers combines anionic polymerization techniques with CRP methods and anionic ring-opening polymerization using azide-alkyne Huisgen cycloaddition as the ligation method. For this purpose, we successfully employed our alkyne-modified DPE derivative in sequential anionic polymerization. In the case of methacrylate-type monomers welldefined alkyne midfunctional diblock copolymers consisting of a first block of PB and a second block of either PtBMA or PDMAEMA were synthesized. Click reactions with azidofunctionalized perylene bisimide verified the successful incorporation of only one DPE unit at the block junction. In contrast to other DPE derivatives, we observed that click-DPE can copolymerize with 2VP, which offers the advantage of producing alkyne mid-functionalized diblock copolymers with P2VP as first block and a methacrylate as second block. Therefore, 2VP and butadiene and styrene and their derivatives can be used as first blocks and methacrylate type monomers as second block to obtain well-defined diblock copolymers bearing an alkyne function at the block junction. By using a toolbox of different azido-functionalized homopolymers, we demonstrate that a variety of well-defined ABC miktorarm star terpolymers is accessible via this modular approach. These exhibited monomodal molecular weight distributions with small disperisties close to 1.10 or even lower.

The obtained miktoarm star terpolymers are interesting new polymers regarding their bulk morphologies and solution-based self-assembly. Results from the self-assembly of these ABC miktoarm star terpolymers will be reported in subsequent publications. A further advantage is that due to the use of anionic polymerization miktoarm star terpolymers with a polybutadiene block are accessible, which can afterward be functionalized through thiol—ene click chemistry⁵⁴ or used for

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selective cross-linking.^{5,55} Furthermore, the ABC miktoarm star terpolymer containing arms of polybutadiene, poly(N,Ndimethylaminoethyl methacrylate) and poly(ethylene oxide) is a promising candidate in the field of biotechnological applications like gene delivery.^{56–58} Our approach enables the upscaling of the synthesis of ABC miktoarm star terpolymers to more than 1 g. Both synthetic steps for diblock and homopolymer synthesis are well-established polymerization methods, and no further complex synthetic procedures are necessary, as compared to other methods. Because of the strong versatility of click chemistry and the increasing amount of publications dealing with it, we expect our click-DPE to offer a variety of new possibilities in the design of novel custom polymer architectures and materials.

ASSOCIATED CONTENT

S Supporting Information

Materials section, polymerization procedures, characterization section, characterization of ω -azido homopolymers, click reaction with poly(*tert*-butyl methacrylate) and discussion of the reactivity of click-DPE toward living P2VP-Li; UV–vis spectra of perylene-labeled diblock copolymers, SEC traces of polybutadiene precursors, poly(ethylene oxide) and click reactions, MALDI-ToF mass spectra of polybutadiene precursors and an exemplarily ¹H NMR spectrum of μ -BT1S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Hadjichristidis, N. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 857–871.

- (2) Hückstädt, H.; Göpfert, A.; Abetz, V. Macromol. Chem. Phys. 2000, 201, 296-307.
- (3) Junnila, S.; Houbenov, N.; Hanski, S.; Iatrou, H.; Hirao, A.; Hadjichristidis, N.; Ikkala, O. *Macromolecules* **2010**, *43*, 9071–9076.
- (4) Matsushita, Y.; Hayashida, K.; Takano, A. Macromol. Rapid Commun. 2010, 31, 1579–1587.
- (5) Walther, A.; Yuan, J.; Abetz, V.; Müller, A. H. E. *Nano Lett.* **2009**, *9*, 2026–2030.
- (6) Song, J.; Shi, T.; Chen, J.; An, L. J. Phys. Chem. B 2010, 114, 16318-16328.

- (7) Li, Z.; Hillmyer, M. A.; Lodge, T. P. Langmuir 2006, 22, 9409–9417.
- (8) Li, Z.; Hillmyer, M. A.; Lodge, T. P. Nano Lett. 2006, 6, 1245–1249.
- (9) Iatrou, H.; Hadjichristidis, N. Macromolecules 1992, 25, 4649-4651.
- (10) Sioula, S.; Tselikas, Y.; Hadjichristidis, N. *Macromolecules* **1997**, 30, 1518–1520.
- (11) Mavroudis, A.; Hadjichristidis, N. Macromolecules 2005, 39, 535–540.
- (12) Fujimoto, T.; Zhang, H.; Kazama, T.; Isono, Y.; Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, *33*, 2208–2213.
- (13) Hückstädt, H.; Abetz, V.; Stadler, R. Macromol. Rapid Commun. 1996, 17, 599-606.
- (14) Quirk, R. P.; Yoo, T.; Lee, B. J. Macromol. Sci. 1994, 31, 911-926.
- (15) Lambert, O.; Dumas, P.; Hurtrez, G.; Riess, G. Macromol. Rapid Commun. 1997, 18, 343–351.
- (16) Lambert, O.; Reutenauer, S.; Hurtrez, G.; Riess, G.; Dumas, P. Polym. Bull. 1998, 40, 143-149.
- (17) Saito, N.; Liu, C.; Lodge, T. P.; Hillmyer, M. A. Macromolecules 2008, 41, 8815–8822.
- (18) Li, Z.; Hillmyer, M. A.; Lodge, T. P. Macromolecules 2004, 37, 8933-8940.
- (19) Liu, C.; Hillmyer, M. A.; Lodge, T. P. Langmuir 2009, 25, 13718–13725.
- (20) Abouelmagd, A.; Sugiyama, K.; Hirao, A. *Macromolecules* **2011**, 44, 826–834.
- (21) Matyjaszewski, K.; Tsarevsky, N. V. Nat. Chem. 2009, 1, 276–288.
- (22) Gregory, A.; Stenzel, M. H. Prog. Polym. Sci. 2012, 37, 38-105.
- (23) Huisgen, R. Angew. Chem., Int. Ed. 1963, 2, 633-645.
- (24) Binder, W. H.; Sachsenhofer, R. Macromol. Rapid Commun. 2008, 29, 952-981.
- (25) Huisgen, R. Angew. Chem., Int. Ed. 1963, 2, 565-598.
- (26) Liu, H.; Li, C.; Liu, H.; Liu, S. Langmuir 2009, 25, 4724-4734.
- (27) Zhang, Y.; Liu, H.; Dong, H.; Li, C.; Liu, S. J. Polym. Sci., Part A:
- Polym. Chem. 2009, 47, 1636-1650.
- (28) Khanna, K.; Varshney, S.; Kakkar, A. *Macromolecules* **2010**, *43*, 5688–5698.
- (29) Iskin, B.; Yilmaz, G.; Yagci, Y. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 2417–2422.
- (30) Zhang, Y.; Li, C.; Liu, S. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 3066–3077.
- (31) Gunay, U. S.; Durmaz, H.; Gungor, E.; Dag, A.; Hizal, G.; Tunca, U. J. Polym. Sci., Part A: Polym. Chem. 2011, 729-735.
- (32) Wong, E. H. H.; Stenzel, M. H.; Junkers, T.; Barner-Kowollik, C. *Macromolecules* **2010**, *43*, 3785–3793.
- (33) Wang, G.; Luo, X.; Liu, C.; Huang, J. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 2154–2166.
- (34) Ye, C.; Zhao, G.; Zhang, M.; Du, J.; Zhao, Y. *Macromolecules* **2012**, 45, 7429–7439.
- (35) Schlosser, M.; Schaub, B. Chimia 1982, 36, 396-397.
- (36) Tsuda, K.; Ishizone, T.; Hirao, A.; Nakahama, S.; Kakuchi, T.; Yokota, K. *Macromolecules* **1993**, *26*, 6985–6991.
- (37) Auschra, C.; Stadler, R. Polym. Bull. 1993, 30, 257-264.
- (38) Ishizone, T.; Uehara, G.; Hirao, A.; Nakahama, S.; Tsuda, K. *Macromol. Chem. Phys.* **1998**, 199, 1827–1834.
- (39) Quirk, R.; Yoo, T.; Lee, Y.; Kim, J.; Lee, B. Adv. Polym. Sci. 2000, 153, 67–162.
- (40) Waack, R.; Doran, M. A. J. Am. Chem. Soc. 1969, 91, 2456-2461.
- (41) Giebeler, E.; Stadler, R. Macromol. Chem. Phys. 1997, 198, 3815-3825.
- (42) Lang, A. S.; Neubig, A.; Sommer, M.; Thelakkat, M. *Macromolecules* **2010**, *43*, 7001–7010.
- (43) Hsieh, H. L.; Quirk, R. P. In Anionic Polymerization: Principles and Practical Applications; Marcel Dekker: New York, 1996.

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Macromolecules

(44) Gondi, S. R.; Vogt, A. P.; Sumerlin, B. S. Macromolecules 2007, 40, 474-481.

- (45) Mantovani, G.; Ladmiral, V.; Tao, L.; Haddleton, D. M. Chem. Commun. 2005, 2089–2091.
- (46) Reinicke, S.; Schmalz, H. Colloid Polym. Sci. 2011, 289, 497–512.

(47) Coessens, V.; Matyjaszewski, K. J. Macromol. Sci. 1999, 36, 667–679.

(48) Barner-Kowollik, C.; DuPrez, F. E.; Espeel, P.; Hawker, C. J.; Junkers, T.; Schlaad, H.; VanCamp, W. Angew. Chem., Int. Ed. 2011, 50, 60–62.

(49) Durr, C. J.; Emmerling, S. G. J.; Lederhose, P.; Kaiser, A.; Brandau, S.; Klimpel, M.; Barner-Kowollik, C. *Polym. Chem.* **2012**, *3*, 1048–1060.

(50) Inglis, A. J.; Pierrat, P.; Muller, T.; Brase, S.; Barner-Kowollik, C. Soft Matter **2010**, *6*, 82–84.

(51) Zhong, M.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 2668–2677.

(52) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. Macromolecules 1983, 16, 214–220.

(53) Plamper, F. A.; Schmalz, A.; Penott-Chang, E.; Drechsler, M.; Jusufi, A.; Ballauff, M.; Müller, A. H. E. *Macromolecules* **200**7, *40*, 5689–5697.

(54) Justynska, J.; Hordyjewicz, Z.; Schlaad, H. Polymer 2005, 46, 12057–12064.

(55) Walther, A.; Goldmann, A. S.; Yelamanchili, R. S.; Drechsler, M.; Schmalz, H.; Eisenberg, A.; Müller, A. H. E. *Macromolecules* **2008**, *41*, 3254–3260.

(56) van de Wetering, P.; Cherng, J.-Y.; Talsma, H.; Hennink, W. E. J. Controlled Release **1997**, 49, 59–69.

(57) Schallon, A.; Jérôme, V.; Walther, A.; Synatschke, C. V.; Müller, A. H. E.; Freitag, R. *React. Funct. Polym.* **2010**, *70*, 1–10.

(58) Majewski, A. P.; Schallon, A.; Jérôme, V.; Freitag, R.; Müller, A. H. E.; Schmalz, H. Biomacromolecules 2012, 13, 857-866.