Macromol. Symp. **2009**, 275-276, 13–23 DOI: 10.1002/masy.200950102

Synthesis of Reactive Triblock Copolymers via Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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Summary: ABA and BAB triblock copolymers of vinylbenzyl chloride and styrene with low polydispersity and different block lengths and block length ratios were produced via reversible addition fragmentation chain transfer (RAFT) polymerization. The used RAFT agent butan-1,4-diyl-bis(1-phenylethyl)trithiocarbonate is a Z-connected bis-RAFT-agent, that allows the synthesis of triblock copolymers in only two steps. The polyvinylbenzyl chloride blocks were quantitatively converted into polyamine blocks by reaction with diethyl amine. All the synthesized block copolymers are microphase separated polymers.

Keywords: block copolymers; hydrophilic polymers; microphase separated polymers; poly(vinylbenzyl chloride) (PVBC); reversible addition fragmentation chain transfer (RAFT)

Introduction

Controlled free radical polymerization techniques, such as nitroxide-mediated radical polymerization[1,2] (NMRP), atom transfer radical polymerization[3] (ATRP) and reversible addition fragmentation transfer[4,5] (RAFT) provide the opportunity to prepare a variety of well-defined macromolecules with designed architectures. The radical nature of the intermediates create these methods very chemoselective, allowing polymerization in the presence of many functionalities without the need for protecting groups. These ‘‘living’’ techniques provide control about the molecular weight of the resulting polymers and maintain low polydispersities.[6,7] The use of unimolecular initiators allows for the preparation of a variety of morphologies including linear polymers, graft polymers and star polymers.

RAFT polymerization is recognized as one of the most versatile methods for block copolymer synthesis and numerous examples of block synthesis have now appeared in the literature. Of considerable interest has been the ability to make hydrophilic/hydrophobic or double hydrophilic block copolymers where the hydrophilic block is composed of unprotected polar monomers such as amine-based monomers.

RAFT agents are generally not compatible with primary and secondary amino or with thiol functionality, but Armes and coworkers [8] have recently shown that RAFT is possible with primary amino functionality as long as it is fully protonated (in 2-aminoethyl methacrylate).

Use of a bis-RAFT agent allows the direct synthesis of triblock copolymers in a ‘one-pot’ reaction (ABA or BAB). The RAFT agent functionalities may be connected through the ‘Z’ or ‘R’ groups. Symmetrical monotrithiocarbonates can be considered to be in the class of ‘Z-connected’ bis-RAFT agents.

In our work for synthesis of membranes for fuel cells by radiation induced graft polymerization[9] vinylbenzyl chloride (VBC) is an important precursor in the synthesis of functionalized polymers. In [10] a larger variety of polycations can be derived from well-defined poly(vinylbenzyl chloride)

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precursors. The vinylbenzyl chloride blocks were synthesized by NMRP and quantitatively converted into cationic polyelectrolytes by reactions with tertiary amines.

Here we report on the synthesis of AB diblock, ABA and BAB triblock copolymers containing hydrophilic/hydrophobic blocks including the following steps:

1. Synthesis of block copolymers of VBC and styrene with a narrow molecular weight distribution by RAFT controlled free radical polymerization.
2. Quantitative modification of the reactive VBC-block into amine structures.

Our RAFT agents are ‘Z-connected’ mono- and bis-RAFT agents as illustrated in Scheme 1.

Experimental Part

Chemicals

Styrene (Fluka) was distilled under reduced pressure. Vinylbenzyl chloride (VBC) (Fluka) was purified by passing through a inhibitor remover column. 2,2′-azobis (isobutyronitrile) (AIBN) was recristallized before use. Hexanethiol, 1,4-butanedithiol, carbon disulfide, 1-bromoethyl benzene, diethylamine and triethylamine were used without further purification.

Synthesis of Hexyl-1-phenylethyltrithiocarbonate (HPTTC)

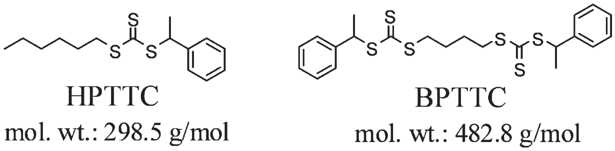
10 mmol of hexanethiol (1.18 g, 1.41 mL) was dissolved in 50 mL of $CHCl_3$. 1.2 eq. of triethylamine (1,23 g, 1.70 mL) were added to this solution. After 1 hour CS_2 was added in excess (~5 mL). This step leads to a yellow color of the solution. After another 15 minutes 1,2 eq. of 1-bromoethyl benzene (2.31 g, 1.7 mL) were added to the solution. This solution was stirred at room temperature for 15 hours. After that the organic phase was washed one time with diluted HCl and two times with distilled water. It was than dried over Na_2SO_4. The chloroform was removed from the reaction mixture by using a rotary evaporator. The remaining reactants and side products were removed by means of a very high vacuum. In this process the product was cautiously heated from time to time. The product was obtained as a yellow liquid (2.99 g, 100%).

^{1}H-NMR ($CDCl_3$) δ (ppm): 0,84–0,91 (t, 3 H); 1,27–1,31 (m, 4 H); 1,63–1,76 (m, 5 H); 2,02–2,15 (t, 2 H); 3,28–3,35 (t, 2H); 5,28–5,38 (q, 1 H); 7,23–7,36 (m, 5 H,).

^{13}C-NMR ($CDCl_3$) δ (ppm): 14,1; 21,4; 22,5; 28,0; 28,6; 31,3; 36,8; 50,1; 126,8; 127,7; 128,7; 141,2; 223,0.

Synthesis of Butan-1,4-diyl-bis (1-phenylethyl)trithiocarbonate (BPTTC)

1,4-butanedithiol (10 mmol, 1.22 g, 1.17 mL) was dissolved in 50 mL of chloroform. Triethylamine (2.4 eq., 2.47 g, 3.4 mL) was added and the solution was stirred for 1 hour. Carbon disulfide in excess (~5 mL) and, after another 15 minutes, 2,4 eq. of 1-bromoethyl benzene (4.61 g, 3.4 mL) were added to this solution. The reaction mixture was stirred for 15 hours. The organic phase was washed one time with diluted HCl and two times with distilled water. The solution was dried over Na_2SO_4 and the chloroform was removed by means of a rotary evaporator. The remaining reactants and side products were removed by using a very high vacuum. In this process



Scheme 1.

RAFT agents, hexyl-1-phenylethyltrithiocarbonate (HPTTC), butan-1,4-diyl-bis(1-phenylethyl)trithiocarbonate (BPTTC).

the product was cautiously heated from time to time. The product was obtained as an orange, high viscous liquid (4.83 g, 100%).

^{1}H-NMR ($CDCl_3$) δ (ppm): 1,71–1,75 (d, 6 H); 2,01–2,06 (t, 4 H); 3,28–3,35 (t, 4 H); 5,26–5,37 (q, 2 H); 7,23–7,37 (m, 10 H).

^{13}C-NMR ($CDCl_3$) δ (ppm): 21,4; 27,4; 35,9; 50,2; 127,8; 128,7; 141,1; 222,5.

Polymerizations

The RAFT agent and the initiator (AIBN) were dissolved in the monomer. All polymerizations were carried out in bulk with 30 mmol/L AIBN as initiator in sealed 10 mL glass vials under nitrogen atmosphere. They were heated in a block heater at 70 °C. After preset times the vials were removed from the heater and cooled down in an ice bath. The samples were diluted with THF and precipitated in methanol. The polymers were dried at 50 °C.

Block Copolymerizations

The Macro-RAFT agent and the initiator were dissolved in the comonomer. The further procedure is equivalent to polymerization.

Amination of the Block Copolymers

1 g of the block copolymer was filled into a glass vial and dissolved with 7 mL of THF. 2 mL of diethyl amine (excess) were added and the solution was sealed and heated for 5 hours in a block heater at 70 °C. The polymers were precipitated in aqueous methanol (MeOH: $H_2O = 50:50$) and dried at 50 °C.

Molecular weights were determined via size exclusion chromatography (SEC) measurements which were carried out on a KNAUER size exclusion chromatograph in tetrahydrofurane (THF) at 25 °C. Polystyrene standards were used for calibration.

Glass-transition temperatures were measured in a differential scanning calorimeter DSC 25 (METTLER TOLEDO).

FTIR spectra were recorded by using a IR-spectrometer BIORAD, model FTS 7000 with a photoacoustic cell MTEC, model 300. A graphite sample was used as background.

Results and Discussion

RAFT agents

In this work we used two RAFT agents: the monofunctional hexyl-1-phenylethyltrithiocarbonate (HPTTC) and the bifunctional butan-1,4-diyl-bis(1-phenylethyl)trithiocarbonate (BPTTC). The main focus lies on the bifunctional BPTTC, because it is suitable for a two-step synthesis of triblock copolymers. HPTTC was used to proof the reactivity of both functionalities of BPTTC. The great advantages of these trithiocarbonates are simple syntheses, quantitative yields and good purities.

RAFT-Polymerization of Styrene and Vinylbenzyl Chloride

Figure 1 shows the typical evolution of the molecular weight (M_n) and of the polydispersity as a function of monomer conversion of both monomers with the bis-RAFT agent BPTTC. The RAFT agent concentration was 15 mmol/L for all reactions. For both monomers a linear increase of the molecular weights with the monomer conversion takes place, revealing the controlled character of this polymerizations. The polydispersities are about 1.2 for PS and about 1.3 for P(VBC). The molecular weights of P(VBC) are little higher than the molecular weights of styrene at the same conversion, due to the higher molecular weight of VBC

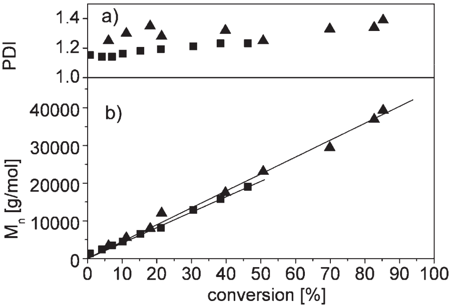


Figure 1.

Plots of M_w/M_n (a) and M_n (b) vs. conversion for styrene (!) and VBC (7) polymerization in presence of bis-RAFT agent BPTTC (15 mmol/L), initiator AIBN (30 mmol/L), T = 70°C.

(M(S) = 104.15 g/mol, M(VBC) = 152.62 g/mol). Polystyrene standards were used for the two monomers. The result points toward similar hydrodynamic volumes of PS and P(VBC).

Some selected conversion-scaled molecular weight distributions of styrene and VBC polymerization are shown in Figure 2. The bis-RAFT agent BPTTC is an efficient RAFT agent for S und VBC.

The PS and P(VBC) polymers have a low polydispersity even at high conversion. The time dependence of the monomer conversion is shown in Figure 3a. The polymerization of VBC shows a higher polymerization rate than the polymerization of styrene. After 300 minutes about 85% of VBC but only about 46% of styrene are converted. The bruttopolymerization rates for reaction temperature T = 70 °C are 11%/h for styrene and 28%/h for VBC. There is the following explanation for it, due to the electron-withdrawing substituent on the styrene ring (CH_2Cl), the polymerization rates are increased in comparison to similar controlled styrene polymerizations. This rate enhancement corresponds to the previously reported substituent effect for conventional free radical polymerization [11] and is in good agreement with our former investigations of the p-chlorstyrene block copolymerization via NMRP.[12]

In all cases the polymerization rate is approximately first order with respect to monomer concentration, indicating a steady state for propagating radicals within the studied range of conversion. The linear relationship between $\ln([M_0]/[M])$ and polymerization time can be observed in Figure 3b. All the evidence indicates that

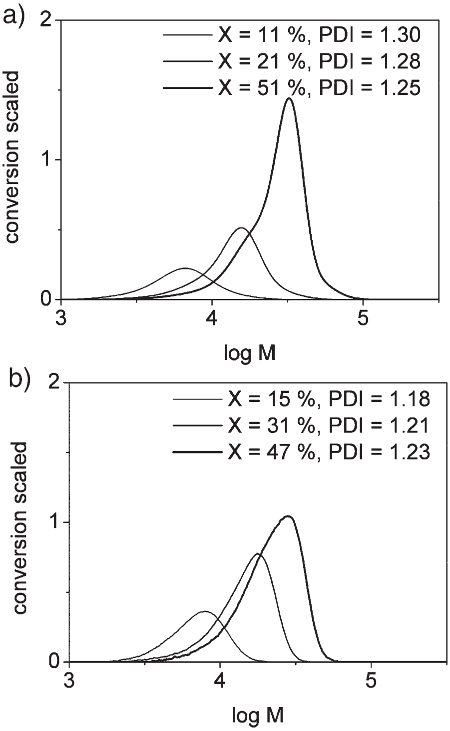


Figure 2.
a) Conversion-scaled molecular weight distribution of a) styrene and b) VBC polymerization at 70 °C with 15 mmol/g bis-RAFT agent BPTTC and 30 mmol/L AIBN, Reaction times a) up to 300 min and b) up to 120 min reaction time.

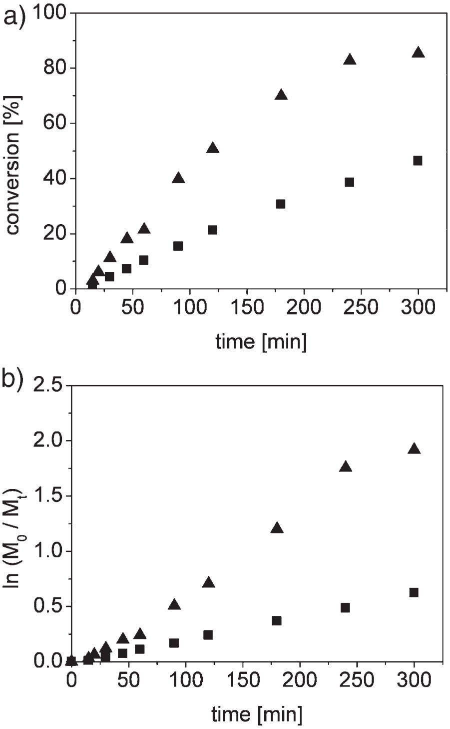
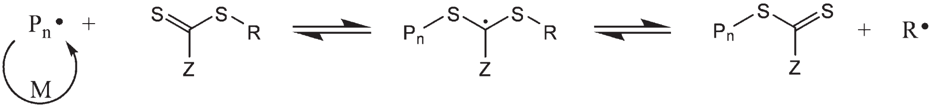


Figure 3.
a) Conversion-time-plot, b) $\ln([M_0]/[M])$-time-plot for styrene (■) and VBC (▲) polymerization with 15 mmol/g bis-RAFT agent BPTTC and 30 mmol/L AIBN at 70 °C in bulk.



Scheme 2.
Start-mechanism of RAFT polymerization.

the polymerizations of S and VBC are controlled free radical processes.

The start of the RAFT-polymerization shows the reversible chain transfer reaction in Scheme 2.

The rate of activation of the initial RAFT agent is very important with regard to effective control of the polymerization. The initialization periods of our mono-RAFT agent HPTTC are represented into Figure 4a for the Styrene and VBC polymerization. The time-dependence of the concentration of the RAFT agent at the beginning of the reaction was determined experimentally by SEC.[13] The free RAFT agent HPTTC is exhausted completely after 25 to 35 minutes. An induction phase occurs only until this time. No retardation can be observed, after that, see Figure 4b.

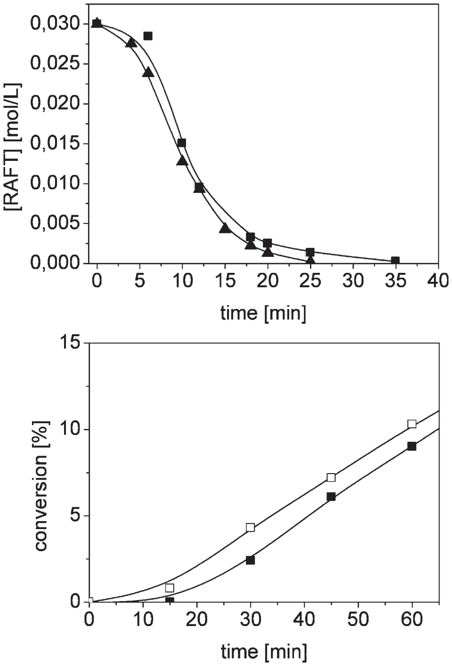


Figure 4.
a) RAFT agent HPTTC concentration vs reaction time for styrene (■) and VBC (▲), [HPTTC] = 30 mmol/L, b) conversion vs reaction time plot for styrene with HPTTC (■) and BPTTC (□), [HPTTC] = 30 mmol/L, [BPTTC] = 15 mmol/L, [AIBN] = 30 mmol/L at 70 °C in bulk.

We characterized the RAFT initialization following the concept of Rizzardo et al.[4] by determining the transfer coefficients $C_{tr} = k_{tr}/k_p$. This is a simplification for very active RAFT agents. A plot of log ([M]) vs log([RAFT]) should be a straight line with the slope proving the transfer constant. The transfer constants for HPTTC are c_{tr} (S) = 117 and c_{tr} (VBC) = 80. The difference between Styrene and VBC explains itself by the higher polymerization rate of of VBC, this means k_p is higher in $C_{tr} = k_{tr}/k_p$.

Propagation of both RAFT Functionalities

An important requirement for the synthesis of triblock copolymers is that the propagation occurs on both functionalities of the RAFT agent. An exact proof of chain growth at both sides gives a polymerization with a mixture of mono- and biradical RAFT agents. To proof this, polymerizations of styrene and VBC were performed with the bifunctional BPTTC and the monofunctional HPTTC together. The HPTTC: BPTTC ratio was 2:1 (30 mmol/L:15 mmol/L). Figure 5 shows the conversion-scaled molecular weight distributions of styrene (5a) and VBC (5b) polymerization with both RAFT agents. In this experiments, the kinetic conditions are equal for all chain ends. Thus, the biradical chains are always twice as long as the monoradical chains. With increasing conversion, the difference between the two species and the bimodality of the curves in Figure 5 becomes more and more distinguishable. According to the RAFT agent ratio, the mass fractions of the two species are nearly equal.

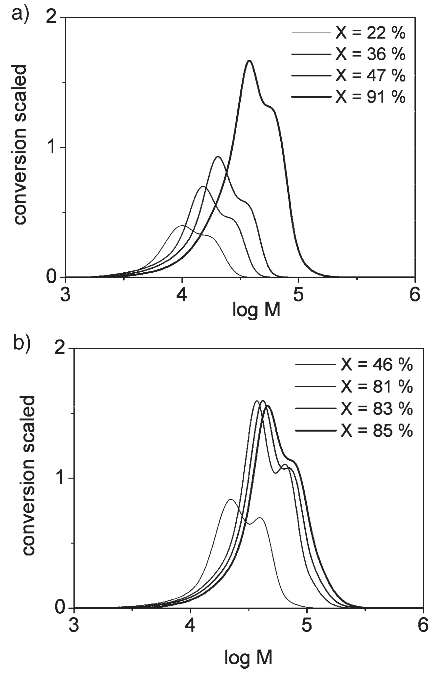


Figure 5.
Conversion-scaled molecular weight distributions of a) styrene and b)VBC, polymerization with 30 mmol/L HPTTC,15 mmol/L BPTTC and 30 mmol/L AIBN at 70 °C in bulk.

The experiments in Figure 5 lead to the conclusion, that both functionalities of BPTTC undergo polymerization with the same reactivity.

Synthesis of Triblock Copolymers with PS and P(VBC) Blocks

An important criterion of living polymerization is the capacity to add further monomer, either to extend the kinetic chain length of a homopolymer or add a different monomer to form a block copolymer. For checking the chain extension, the polymerization of PS produced in the presence of BPTTC is continued. This PS (Macro-RAFT) was heated with new styrene and new initiator, following the standard procedure for the polymerizations. Figure 6 shows the molecular weight distributions of the used PS sample and the chain extension. The polymer after the chain extension shows a unimodal distribution with no significant shoulder that is shifted to higher weights. The polydispersities increases from 1.23 for the starting PS sample up to 1.48.

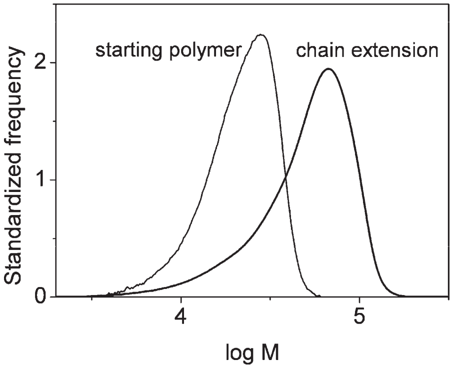


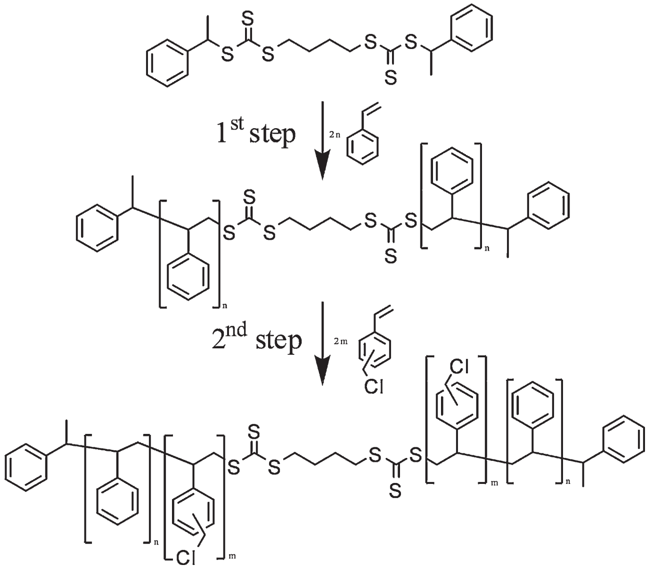
Figure 6.
Molecular weight distributions of polystyrene before and after chain extension. Starting polymer: $M_n =$ 18900 g/mol, PDI = 1.23; extended polymer: $M_n =$ 38900 g/mol, PDI = 1.48.

ABA- and BAB-triblock copolymers can be controlled polymerized in a two step synthesis by using the bis-RAFT agent BPTTC. BPTTC is a "Z-connected" bis-RAFT agent, this means the propagating radicals are linear chains that are dissociated from the core and the thiocarbonylthio functionality is retained at the inside, see Scheme 3. In this work A is styrene and B is VBC, so that ABA is PS-b-P(VBC)-b-PS and BAB is P(VBC)-b-PS-b-P(VBC).

In the first step the so called Macro-RAFT agent is synthesized. We have synthesized Macro-RAFT agents consisting of styrene or VBC each with molecular weights of about 10000 g/mol, 20000 g/mol and 30000 g/mol. The experimental data of these polymers are shown in Table 1, the molecular weight distributions are shown in Figure 7.

Due to the use of a Z-linked RAFT agent, the polymer chains of these Macro-RAFT agents become the side blocks in the triblock copolymer. The half of the molecular weight of the Macro-RAFT is the molecular weight of every side block.

The polymerization using VBC- or styrene-Macro-RAFT of different molecular



Scheme 3.
Synthesis of triblock copolymers PS-b-P(VBC)-b-PS (ABA) from "Z-connected" bis-RAFT agent BPTTC.

weights, comonomer and new initiator results in triblock copolymers with variable block length ratio. This new comonomer builds the middle block of the triblock copolymer. The Macro-RAFT concentration was chosen 15 mmol/L for PS Macro-RAFT and 10 mmol/L for P(VBC) Macro-RAFT. The molecular weights and polydispersities of these block copolymers were determined by means of SEC (Table 2). Some typical molecular weight distributions are drawn in Figure 8.

The polydispersities increase with conversion of the comonomer. In most experiments the PDI values rise above 1.5 if the conversion is higher than 70%.

To investigate the microphase behavior, the glass transition temperatures were determined by means of DSC and are

Table 1.
Properties of the used Macro-RAFT agents.

Type	M_n [g/mol]	PDI
Poly(styrene)	12000	1.20
Poly(styrene)	19000	1.25
Poly(styrene)	27800	1.29
Poly(vinylbenzyl chloride)	13000	1.17
Poly(vinylbenzyl chloride)	25400	1.21
Poly(vinylbenzyl chloride)	32600	1.28

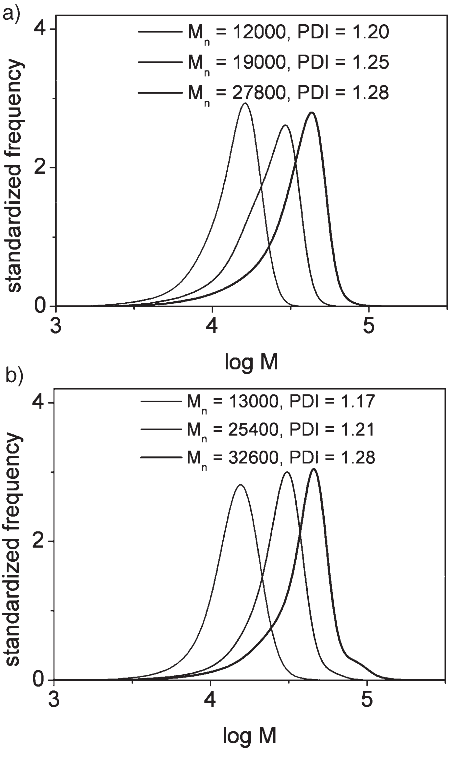


Figure 7.
Molecular weight distributions of all used Macro-RAFT agents. a) styrene Macro-RAFT agents, b) VBC Macro-RAFT agents.

Table 2.
Properties of the block copolymers.

Type (A = S, B = VBC)	$M_{n,\ total}$ [g/mol]	$M_{n,\ middle\ block}$ [g/mol]	$M_{n,\ per\ side\ block}$ [g/mol]	PDI (Makro-RAFT)	PDI (Block copolymer)	reaction time [min]	conversion [%]
ABA	28500	16500	6000	1.20	1.43	105	59
ABA	35200	23200	6000	1.20	1.63	180	80
ABA	38900	26900	6000	1.20	1.86	300	96
ABA	37800	18800	9500	1.25	1.46	105	69
ABA	47500	28500	9500	1.25	1.66	180	94
ABA	52200	33200	9500	1.25	1.75	300	99
ABA	40210	12500	13900	1.29	1.52	105	69
ABA	47900	20100	13900	1.29	1.72	180	75
ABA	50900	23100	13900	1.29	1.94	300	84
BAB	24100	11100	6500	1.17	1.33	140	30
BAB	36800	23900	6500	1.17	1.31	300	53
BAB	60000	47000	6500	1.17	1.38	540	97
BAB	29600	4200	12700	1.21	1.44	140	49
BAB	41100	15700	12700	1.21	1.43	300	72
BAB	61400	36000	12700	1.21	2.11	540	100
BAB	39200	6600	16300	1.28	1.51	140	43
BAB	49400	16800	16300	1.28	1.63	300	62
BAB	74700	42100	16300	1.28	1.84	540	87

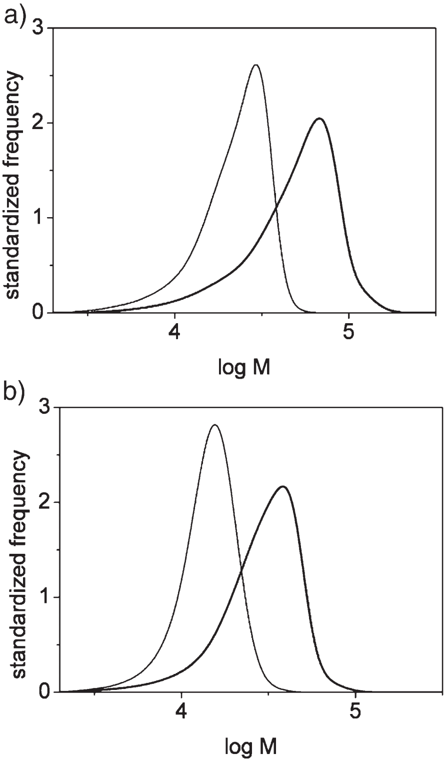


Figure 8.
Comparison of molecular weight distributions of a Macro-RAFT agent and the resulting block copolymer. a) PS → PS-b-P(VBC)-b-PS, b) P(VBC) → P(VBC)-b-PS-b-P(VBC).

shown in Table 3. For all block copolymers two transition temperatures can be found. These temperatures are the glass transition temperatures of the homopolymers, that means a microphase separation of the polymer blocks takes place.

Amination of the Triblock Copolymers

The primary aim of this work was the synthesis of block copolymers containing hydrophilic/hydrophobic or double hydrophilic blocks. Hydrophilic blocks with amino groups in the side chain are very interesting. Monomers with amino groups are bad compatible with the RAFT polymerization, so we chose the way of a polymer analogous substitution of the P(VBC) blocks with amines to poly(vinylbenzyl amine)

Table 3.
Glass transition temperatures of homopolymers, block copolymers and aminated block copolymers. The values were measured by means of DSC.

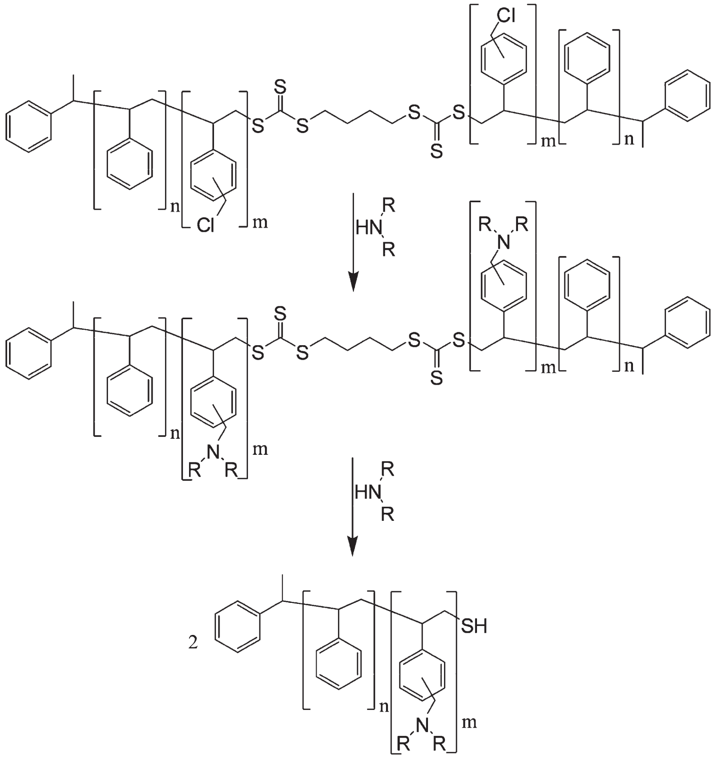
polymer type	T_g [°C]
P(S)	103
P(VBC)	148
P(amine)	162
P(S)-b-P(VBC)-b-P(S)	98 and 150
P(S)-b-P(amine)-b-P(S)	103 and 162
P(VBC)-b-P(S)-b-P(VBC)	93 and 152
P(amine)-b-P(S)-b-P(amine)	101 and 162

blocks. In this paper the reaction of the block copolymers with diethyl amine is discussed. The quantitative reaction of the reactive VBC block by diethyl amine is described in Scheme 4.

The obtained PS/P(amine) block copolymers are "rubber like" when wet and become brittle after drying. The dried polymers were analyzed via DSC and FTIR to examine the success of the substitution. The glass transition temperatures are shown in Table 3. For the PS/P(amine) block copolymers two glass transition temperatures can be found. Only the glass transition temperature of the PS block but not the T_g of the P(VBC) block is found. But a new glass transition temperature is found at $T_{g2} = 162\,^\circ C$. This indicates a successful substitution of the P(VBC) blocks to P(amine) blocks.

The FTIR spectra are very similar for all kinds of blocklength and block arrangement. Figure 9 shows exemplarily the comparison of the FTIR spectra of a P(VBC)-b-PS-b-P(VBC) block copolymer and the aminated block copolymer. There are two points of the spectra that attract attention. They are highlighted in Figure 9. The spectrum of the aminated block copolymer shows additional peaks at 2967 cm^{-1} and 2797 cm^{-1}. These are the signals of the CH_2 and CH_3 groups of the diethyl amino groups. At 1265 cm^{-1} the strong signal of the chlorine group can be found in the spectrum of the unsubstituted block copolymer. This signal has vanished completely in the spectrum of the aminated block copolymer. This entire disappearance indicates a complete substitution of the chlorine groups to diethyl amino groups.

A side reaction takes place at the amination (see Scheme 4). This reaction between thioesters and primary amines is well known to occur rapidly at ambient temperature, which leads to thioamides and thiols.[12–14] For the attainment of an



Scheme 4.
Amination of a PS-b-P(VBC)-b-PS block copolymer by use of diethyl amine.

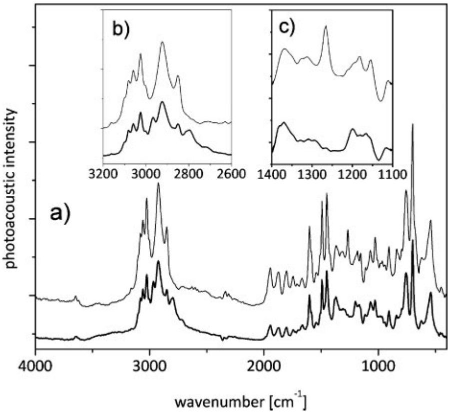


Figure 9.
FTIR sprectra of a P(VBC)-b-PS-b-P(VBC) block copolymer and the resulting aminated block copolymer. a) full spectra, b) new CH_2 and CH_3 bands appear in the sprectrum of the aminated block copolymer, c) chlorine band disappears in the aminated spectrum. — VBC-block copolymer, — aminated block copolymer.

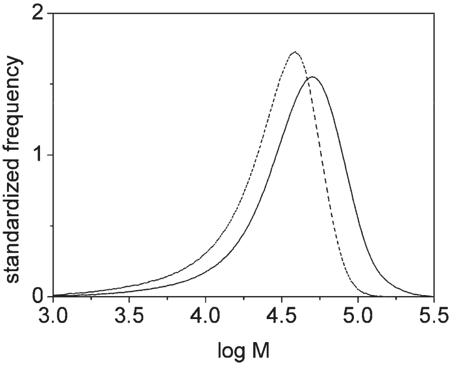


Figure 10.
SEC chromatograms of the triblock copolymer before (—) and after (--) aminolysis with diethylamine without antioxydants.

oxidative coupling of the thiol end groups to disulfide bridges, we worked without nitrogen feed and antioxidant ($Na_2S_2O_4$). The presence or absence of the disulfide species can easily be observed by SEC in the case of triblock copolymers. For the presented triblock copolymers produced from a “Z-connected” bis-RAFT agent, the trithiocarbonate moieties are in the center of the polymer chain (Scheme 4). After the amine treatment we have diblock copolymers with the half the molecular weight of the orginal triblock copolymer or in the case of di-sulfide bridges between two diblock copolymers, we have nearly the molecular weight of the triblock systems.

Figure 10 shows the splitting of the triblock copolymers and no evidence for the formation of disulfide bridges. The qualitative proof of the thiol groups was carried out with a disodium pentacyano nitrosylferrate(III) solution.

The molecular weights (M_n) of the polymers in Figure 10 are 26800 g/mol before and 18100 g/mol after aminolysis. The molecular weight after aminolysis is not exactly 50% of the molecular weight before aminolysis, because of the higher “monomer mass” of vinylbenzyl amin in comparison to vinylbenzyl chloride, but it is obvious, that the triblock copolymers have been split into two diblock copolymers.

With the suggested postpolymerization amination reaction we can produce with Z-group-linked mono-RAFT agents thiol-terminated polyamine diblock copolymers in one step. On the other side arise with R-group-linked bis-RAFT agents an α,ω-thiol functionalized tri-block copolymer with polyamine blocks.

Conclusion

VBC und styrene have been polymerized with narrow molecular weight distributions using mono-RAFT (HPTTC) und bis-RAFT (BPTTC) agents for controlled radical RAFT polymerization. The experimentally derived transfer constants for HPTTC are c_{tr} (S) = 117 and c_{tr} (VBC) = 80. The differences are based on the higher polymerization rate of VBC.

The reactivity of both functionalities of the bis-RAFT agent has been proven by combination of the mono-RAFT and bis-RAFT agents.

The use of the bis-RAFT agent BPTTC allows the synthesis of the triblock copolymers PS-b-P(VBC)-b-PS and P(VBC)-b-PS-b-P(VBC) with different block lengths.

These hydrophobic well defined microphase-separated triblock copolymers can easily be characterized by means of SEC. This is a great advantage for the synthesis of hydrophilic-hydrophobic block copolymers. The successful synthesis and characterization of different triblock copolymers are shown in the present work.

For the synthesis of hydrophilic blocks we used a comparatively simple strategy: a quantitative modification of the reactive VBC blocks with diethyl amine. These modifications lead also to microphase-separated new diblock copolymers PS-b-P(vinylbenzyl amine) with hydrophilic blocks.

The side reaction between the trithiocarbonate and the amine leads irreversibly to thioamides and thiols, this means to a chain splitting into two diblock copolymers. With our reaction conditions we could not reach any oxidative coupling of the thiol end groups to triblock copolymers.

These postpolymerization reaction is a new variable technique to modify VBC block copolymers resulting in new basic or acidic block structures. Besides the opportunity to synthesize block polymers with adjusted block length ratio, we are now able to tune the hydrophobic-hydrophilic balance not only for the whole block copolymer but also for the hydrophilic block itself.

Acknowledgements: The authors acknowledge the Deutsche Forschungsgemeinschaft for financial support within the European Graduate School “Microstructural Control in Free-Radical Polymerization”.

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