Synthesis of Graft Copolymers by Nitroxide Mediated Radical Polymerization of Styrene and *n*-Butylacrylate Using Alkoxyamine-Functionalized Copolymers as Macroinitiators

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Summary: A simple two step method for the preparation of graft copolymers is described in this paper. For the synthesis of the prepolymers the alkoxyaminemonomers 2-methyl-acryli-acid-4-[1-(2,2,6,6-tetramethyl-piperidine-1-yloxy)ethyl]-benzylester(Mas-BzEt-TEMPO) and 2-methyl-acrylic-acid-4-{1-[*N*-tert-butyl-*N*-(1-isopropyl-2-methyl-propyl)-amino-oxy]ethyl}-benzylester (Mas-BzEt-BIPNO) were utilized in radical copolymerizations with styrene, methylmethacrylate, butylmethacrylate and *n*-butylacrylate. These copolymers were then used as multifunctional macroinitiators for nitroxide mediated graft polymerization of styrene and *n*-butylacrylate. The polymerizations were carried out in bulk at 125 °C.

Keywords: alkoxyamine monomer; copolymerization; graft copolymer; nitroxide; radical polymerization

Introduction

There is a great interest in creating specialized copolymers of different architectures for materials with new and improved properties. One of them are graft copolymers which exhibit a good phase separation and are therefore used as compatibilizers, thermoplastic elastomers or polymeric emulsifiers. To synthesize graft copolymers with specific properties structural variables such as the length, property and density of the side chains must be controlled. A suitable method for the preparation of well controlled graft and block copolymers is controlled radical polymerization. Controlled radical polymerization has been achieved by several procedures including nitroxide mediated radical polymerization (NMRP)[1–3], atom transfer radical polymerization (ATRP)[4–6] and reversible addition-fragmentation chain transfer polymerization (RAFT).[7] In the field of graft copolymers mainly ATRP and NMRP have been used.[8] The two main methods to prepare graft copolymers are the living radical polymerization of macromonomers[8] and the grafting from technique where prepolymers are applied as macroinitiators. One suitable method to obtain multifunctional macroinitiators is the application of an alkoxyamine monomer in a radical process. This was first demonstrated by Hawker who applied an alkoxyamine monomer in a radical copolymerization with styrene.[9] Huang et al. also reported about an approach which involved grafting from a copolymer synthesized by the copolymerization of methyl methacrylate (MMA) with an activated ester monomer based on TEMPO.[10] Miura et al. used a prepolymer consisting of MMA and a 4-hydroxy-TEMPO based monomer as macroinitiator for the graft polymerization of styrene and *n*-butylacrylate which were carried in DMF at 125 °C.[11,12] The aim of

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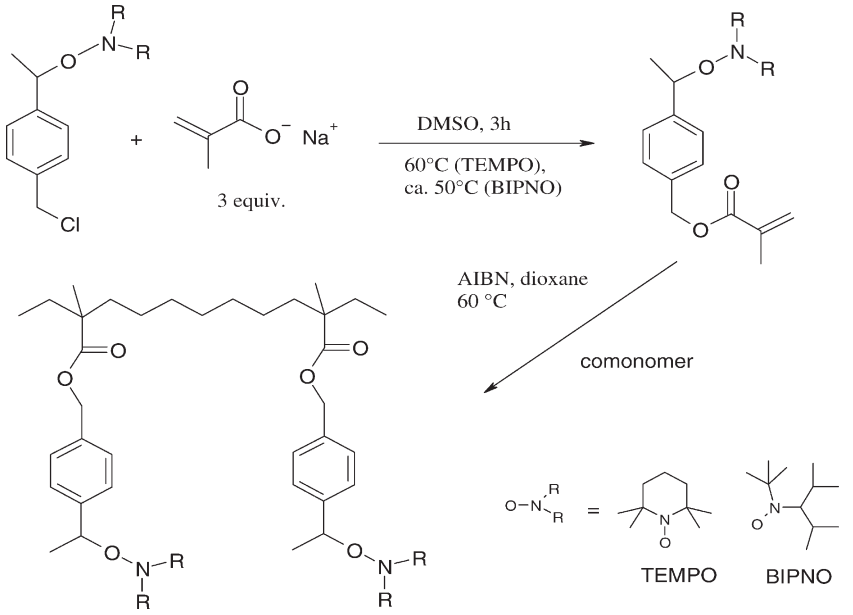

Scheme 1.
Synthesis of the multifunctional macroinitiators.

this paper is the investigation of the graft copolymerization of either styrene or *n*-butylacrylate with different copolymers as macroinitiators. The copolymers were prepared by a free radical process with 2-methyl-acrylic-acid-4-[1-(2,2,6,6-tetramethyl-piperidine-1-yloxy)- ethyl]-benzylester (Mas-BzEt-TEMPO) and 2-methyl-acrylic-acid-4-{1-[*N*-tert-butyl-*N*-(1-isopropyl-2-methyl-propyl)-aminooxy]ethyl}- benzylester (Mas-BzEt-BIPNO) as alkoxyamine monomers (Scheme 1).

Experimental Part

Materials

Styrene (Aldrich), *n*-butylacrylate (Aldrich), *n*-butylmethacrylate (Röhm), methylmeth!acrylate (Röhm) and 4-vinylbenzyl chloride were distilled under reduced pressure. Azo-bis-isobutyronitrile (AIBN) (Merck) was purified by recrystallization from a diethylether/ethanol mixture. For the synthesis of the alkoxyamine monomers sodiummethacrylate (Fluka) and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) (Fluka) were used as received. [N,N′-disalicylidene-1,2-ethanediaminato(2–)]manganese(III)chloride (Mn(salen)Cl) and 1-[1-(4-chloromethyl-phenyl)-ethoxy]-2,2,6,6-tetramethyl-piperidine were synthesized in 84% and 89% overall yield respectively following the procedures given by Bothe.[13] 2,2,5-trimethyl-4-(isopropyl)-3-azahexane-3-oxyl (BIPNO) was synthesized in 39% overall yield as recently published.[14] All other chemicals were used as received. Silica gel for column chromatography was Merck silica gel 60.

Instrumental

Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker DPX 200 spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as reference. Molecular mass distributions were determined by gel permeation chromatography (GPC) on a Knauer instrument equipped with SDV columns of PSS and nucleogel columns of Machery – Nagel with THF as eluent (flow rate: 1 ml/min) and refractive index detection. A calibration curve based on polystyrene standards was used for all samples.

The copolymer compositions were estimated using the nitrogen content which was measured by elemental analysis using a Vario-EL of the company ELEMENTAR-ANALYSEN-SYSTEME GmbH.

Synthesis

Cl-BzEt-BIPNO (1) (N-tert-butyl-O-[1-(4-chloromethyl-phenyl)-ethyl]-N-(1-isopropyl-2-methyl-propyl)-hydroxylamine)

950 mg BIPNO (5.1 mmol) and 1.15 g 4-vinylbenzyl-chloride (7.38 mmol) were dissolved in 7 ml isopropanol in an open flask. The solution was vigorously stirred and 227 mg Mn(Salen)Cl catalyst[14] (0,63 mmol) was added in small portions followed by 313 mg $NaBH_4$ (8 mmol). After stirring the reaction mixture for 24 hours at room temperature it was partitioned between chloroform and 0.5 M HCl. The organic layer was separated and washed with water until it became acid free. It was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (PE:EE 20:1).

Yield: 1.6 g (4.7 mmol, 92%) colourless oil.

$(C_{20}H_{34}ClNO)_n$ $(339.63)_n$: Calcd. C 70.66%, H 10.01%, N 4.11%; Found C 70.89%, H 9.99%, N 4.09%.

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.89-1.28 (m, 21 H) 1.50 (s, 1H), 1.55 (d, 3H), 2.25 (d, 1H), 2.45 (m, 1H), 4.59 (s, 2H), 4.75 (q, 1H), 7.28–7.42 (s, 4H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ 17.74, 18.27, 22.25, 22.82, 23.43, 24.57, 26.91, 27.37, 27.85, 28.17, 29.62, 30.73, 46.23, 59.87, 60.7, 69.52, 69.85, 79.56, 81.09, 126.74, 127.23, 128.24, 135.77, 136.12, 144.57, 144.96.

Mas-BzEt-TEMPO (3) 2-methyl-acrylic-acid-4-[1-(2,2,6,6-tetramethyl-piperidine-1-yloxy)ethyl]-benzylester

1.1 g Cl-BzEt-TEMPO **2** (3.56 mmol) and 1.15 g sodiummethacrylate (10.64 mmol) were dissolved in 60 ml DMSO and stirred for 3 hours at 60 °C. Then 1L of water was added to the reaction mixture and then the solution was extracted three times with 100 ml dichloromethane. The combined organic layers were washed three times with 200 ml water and dried over Na_2SO_4. The solvent was removed under reduced pressure and finally the product was recrystallized from methanol.

Yield: 909 mg (2.5 mmol, 71%) colourless crystals.

$(C_{22}H_{33}NO_3)_n$ $(359.51)_n$: Calcd. C 73.50%, H 9.25%, N 3.90%; Found C 73.70%, H 9.54%, N 3.70%.

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.68/1.02/1.15/1.28 (each br s, 12H), ca. 1.35–1.55 (m, 6H), 1.47 (d, 3H), 1.97 (dd, 3H), 4.82 (q, 1H), 5.19 (s, 2H), 5.58 (quint., 1H), 6.16 (dq, 1H), 7.31 (s, 4H).

Mas-BzEt-BIPNO (4) 2-Methyl-acrylic-acid-4-{1-[N-tert-Butyl-N-(1-isopropyl-2-methyl-propyl)-aminooxy]ethyl}-benzylester

1 g Cl-BzEt-BIPNO **1** (2.9 mmol) and 0.94 g sodiummethacrylate (8.7 mmol) were dissolved in 50 ml DMSO and stirred for 3 hours at 50 °C. Then 900 mL of water was added to the reaction mixture and the solution was extracted three times with 90 ml dichloromethane. The combined organic layers were washed three times with 200 ml water and dried over Na_2SO_4. The solvent was removed under reduced pressure, to give yellow oil as crude product. Purification by flash chromatography (PE:EE 20:1) afforded the product as a colourless oil.

Yield: 654 mg (1.7 mmol, 58%).

$(C_{24}H_{39}NO_3)_n$ $(389)_n$: Calcd. C 73.98%, H 10.01%, N 3.59%, O 12.30%; Found C 74.00%, H 9.91%, N 3.33%, O 12.07%.

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.80–1.25 (m, 21H), 1.49 (s, 1H), 1.51 (d, 3H), 1.97 (s, 3H) 2.25 (d, 2H), 2.45 (m, 1H), 4.65 (q, 1H), 5.16 (s, 2H), 5.55 (d, 1H), 6.15 (d, 1H), 7.32 (s, 4H).

Polymerizations

Preparation of the Prepolymers

For the preparation of the prepolymers Mas-BzEt-TEMPO or Mas-BzEt-BIPNO respectively, the comonomer, dioxane and AIBN were placed in glass ampoules and purged with nitrogen. The ampoules were

Table 1.
Copolymerization of Mas-BzEt-TEMPO with styrene, BuA, BuMA and MMA in dioxane. Reaction temperature is 60 °C, GPC standard is polystyrene.

M1	M2	mol%feed	mol%polymer	AIBN [mmol/L]	t [h]	conv. [%]	Mn [g/mol]	Pd
Mas- T	styrene	5	8	12	22	38	12700	2.29
Mas-T	styrene	10	17	12	22	42	10800	2.4
Mas-T	styrene	20	25	12	22	46	10200	2.53
Mas-T	BuA[1)]	5	6	12	24	86	8600	1.86
Mas-T	BuA	10	9	12	22	78	61400	2.54
Mas-T	BuA	15	15	12	22	68	49100	3.59
Mas-T	BuMA	5	3	12	22	82	41800	2.43
Mas-T	BuMA	10	8	12	22	76	38900	3.05
Mas-T	MMA	10	13	12	22	55	24300	2.67
Mas-T	MMA	20	17	12	24	66	15400	3.48

[1)]THF was used as solvent.

closed gas-tight and heated to 60 °C for a prescribed time. The reaction was terminated by cooling down the samples in a refrigerator. The product was precipitated into methanol and dried in vacuum to constant mass.

Graft Polymerizations on the Prepolymer

For graft polymerizations the respective prepolymer was dissolved in either styrene or *n*-butylacrylate in the desired molar ratio. The solution was purged with nitrogen and put into glass ampoules. The ampoules were closed gas-tight and heated to 125 °C for a prescribed time. After the reaction the samples were cooled down in a refrigerator, diluted with THF and precipitated into methanol. The collected polymer was dried in vacuum to constant mass.

Results and Discussion

Synthesis of the Alkoxyamine Functionalized Copolymers

Copolymerization with Mas-BzEt-TEMPO

First copolymerizations of Mas-BzEt-TEMPO with styrene, butylacrylate, butylmethacrylate and methylmethacrylate with 5 to 30 mol% of the alkoxyamine monomer in the feed were carried out. The copolymerizations were performed under free radical conditions at 60 °C using AIBN as initiator and dioxane as solvent. Generally it could be observed that Mas-BzEt-TEMPO is a suitable monomer for the synthesis of different prepolymers with molecular masses up to 61000 g/mol (Table 1).

The products were characterized with elemental analysis, NMR, GPC, TGA and in some cases with DSC. Figure 1 shows exemplarily the ^{1}H-NMR-spectra of a Poly(Mas-BzEt-TEMPO-co-styrene) polymer in comparison with the NMR-spectra of Mas-BzEt-TEMPO, which is represented as a small picture inside of the figure. After the copolymerization the peaks of the TEMPO units between 0 and 1.5 ppm which belong to the aliphatic protons can be observed. Furthermore the peaks due to the vinylgroup of the monomers at 5.58 and 6.16 ppm disappeared.

With thermogravimetry a thermal degradation step between 230 to 240 °C could be observed, which is characteristically for the degradation of the nitroxide. The copolymer composition has been estimated by elemental analysis; contents of 3 to 25 mol% of the alkoxyaminemonomer could be confirmed. A comparison with the reactivity of MMA showed especially in the case of the copolymerization with styrene that there is no great influence of the bulky substituent on the copolymerization behaviour.

Copolymerization with Mas-BzEt-BIPNO

With the intention to synthesize graft copolymers with polybutylacrylate in the side chain, Mas-BzEt-BIPNO was applied as alkoxyamine monomer in copolymeriza-

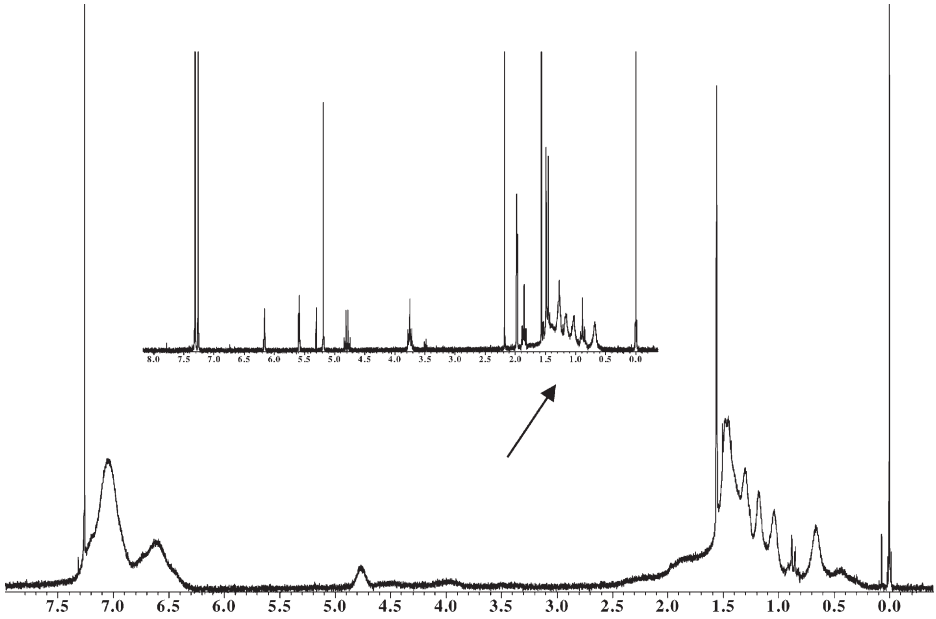

Figure 1.
^{1}H-NMR-spectra of P(Mas-BzEt-TEMPO-co-Styrol) with 19 mol% Mas-BzEt-TEMPO in the copolymer. The small figure illustrates the ^{1}H-NMR-spectra of Mas-BzEt-TEMPO. The arrow indicates the signal structure of the PhEt-TEMPO-unit.

tions with styrene. BIPNO is a new open chain nitroxide which has turned out to be suitable for the controlled radical polymerization of n-butylacrylate.[14] The copolymerizations were also performed under typical free radical conditions with AIBN as initiator and dioxane as solvent at temperatures between 50 and 60 °C (Table 2) and with 5 to 10 mol% of Mas-BzEt-BIPNO in the feed.

As in the case of the copolymerizations with Mas-BzEt-TEMPO the obtained copolymers contained more Mas-BzEt-BIPNO compared to the feed molar ratio. Therefore a significant influence of the substituent on the copolymerization behaviour can also be excluded. However in contrast to Mas-BzEt-TEMPO there is a limit of the molecular masses at 5000 g/mol. The reason for this must be the exchange of the nitroxide. BIPNO is more thermal labile as compared to TEMPO so that it is possible that at elevated temperatures a dissociation of the nitroxide takes place which could lead either to a crosslinking point or to an inhibition of the copolymerization.

Graft Polymerization of Styrene with Mas-BzEt-TEMPO Copolymers as Macroinitiators

In the following step different prepolymers with TEMPO residues were employed as

Table 2.
Copolymerizations of Mas-BzEt-BIPNO (M1) and styrene (M2) with dioxane as solvent under variation of the reaction conditions and the composition in the feed. GPC-standard is polystyrene.

M1 [mol/L]	M2 [mol/L]	AIBN [mmol/L]	T [°C]	t [h]	conv. [%]	M_n [g/mol]	Pd	mol%M1 feed	mol%M1 polymer
0.34	3.06	20	55	24	31	3 900	1.69	10	16
0.12	1.09	12	50	30	11	3 900	1.36	10	16
0.07	1.15	20	55	24	32	5 000	1.58	6	9
0.12	2.3	20	60	10	23	4 600	1.65	5	9

Table 3.
Data of the graft copolymerizations of styrene (St.) with Mas-BzEt-TEMPO-copolymers as backbone (bb) at 125 °C under variation of the macroinitiator concentration, the number of the side chains (amounts of TEMPO in the side chain) and the reaction time. GPC-standard is polystyrene.

backbone	$M_{n,bb}$ [g/mol]	Pd_{bb}	bb [mmol/L]	side chains	$M_{n,\ prod.}$ [g/mol]	$Pd_{\ prod.}$	t [h]	conv. St. [%]
styrene	7200	2.43	10	4	32400	3.81	4	47
styrene	7200	2.43	10	4	47200	2.36	6	57
styrene	6800	2.53	17	4	80500	1.66	8	57
styrene	10200	2.53	3	15	21500	2.81	0.5	7
styrene	10200	2.53	3	15	30200	4.41	2	23
BuA	8600	2.43	10	4	83000	1.39	8	57
BuA	49100	3.59	4	45	76000	4.99	2	6
BuMA	20800	3.62	10	5	100000	3.24	6	56
BuMA	38900	3.05	7	20	52800	4.31	2	11
MMA	22700	2.19	8	15	79700	3.55	8	43
MMA	29700	2.67	2	36	68500	5.43	1.5	18

macroinitiators for the nitroxide mediated graft polymerization of styrene. In this context the influence of the copolymer type, the concentration of the macroinitiator and the amount of the initiating units were investigated. All polymerizations were carried out in bulk at 125 °C for the prescribed reaction time. The purified graft copolymers were characterized in detail with GPC and in some cases with DSC. Table 3 shows the data of the graft polymerizations.

For all experiments an increase of conversion and the molecular masses with time could be observed with a limitation of conversion at 57% after 6 hours. Except from the experiments where backbones with a higher amount of initiating units were used the molecular masses increased without a significant increase of the polydispersities. In a few cases even a slight decrease of the polydispersities could be observed with increasing molecular mass. For a better evaluation of the grafting results the molecular weight distributions of the products were considered in comparison with the prepolymers. Figure 2 shows exemplarily the molecular mass distributions of graft polymers obtained from a Mas-BzEt-TEMPO/styrene copolymer and a Mas-BzEt-TEMPO/butylacrylate copolymer with low molecular masses (6800 and 8600 g/mol). Considering the molecular weight distributions it could be established that graft polymerizations proceeded in a living manner with macroinitiators of molecular weights up to 10000 g/mol and with less than ten initiating units. Only peaks attributed to the graft copolymers can be observed and no trace is left for the macroiniators. When prepolymers with molecular masses higher than 20000 g/mol were used the molecular weight distributions showed small shoulders attributed to products of termination side reaction.

Graft Polymerization of *n*-Butylacrylate with Mas-BzEt-BIPNO Copolymers as Macroinitiators

By the use of P(Mas-BzEt-BIPNO-*co*-styrene) as prepolymers graft polymers with polybutylacrylate as side chains can be synthesized. The applied copolymers have chain lengths which do not exceed a molecular mass of 5000 g/mol and an average amount of initiating units of three, so that the products show a star-like shape. Polymerizations were carried out in bulk at 125 °C under variation of the concentration of the backbones. Additionally 5 mol% of BIPNO with respect to the concentration of the alkoxyamine groups in the copolymer were added to the reaction mixture, to prevent and overly fast and uncontrolled start of the polymerization. Like the products obtained from Mas-BzEt-TEMPO backbones the polymers were characterized in detail with GPC. Table 4 summarizes the results of the graft polymerizations.

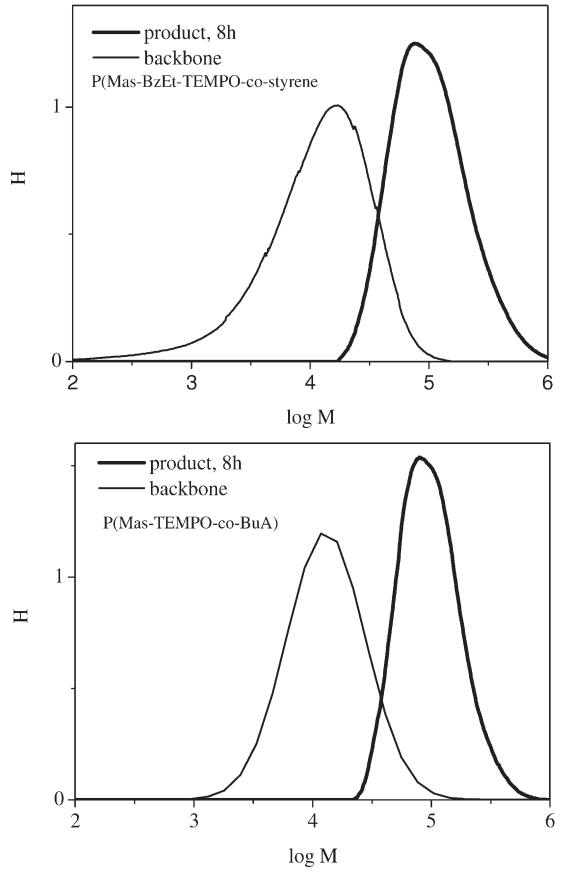

Figure 2.
Molecular weight distribution of the graft polymer (80500 g/mol) obtained from the Mas-BzEt-TEMPO-co-styrene prepolymer (6800 g/mol) and of the graft polymer (83000 g/mol) obtained from the Mas-BzEt-TEMPO-

It could be established that the procedure for the graft polymerization of styrene could be successfully transferred to the graft polymerization of n-butylacrylate. In any case an increase of the molecular mass could be observed without a significant increase of the polydispersity.

Figure 3 shows these exemplarily for two products after 4 and 6 hours reaction time.

It has to be taken from the molecular weight distribution in Figure 3 that at the two experiments a complete incorporation of the macroinitiator has been carried out. For the experiment with 12 mmol/L of macroinitiator concentration a product was formed after 6 h reaction time with a molecular weigth of Mn = 64900 g/mol and a polydispersity of 1.97.

Table 4.
Graft polymerization of n-butylacrylate at 125 °C with P(Mas-BzEt-BIPNO-co-styrene) as backbone (bb) and various number of the side chains (amounts of BIPNO in the side chain), GPC standard is polystyrene.

$M_{n,bb}$ [g/mol]	Pd_{bb}	C_{bb} [mmol/L]	side chains	$M_{n,prod.}$ [g/mol]	$Pd_{prod.}$	t [h]	conv. (BuA) [%]
4000	2.16	12	3	59600	1.96	6	56
4000	1.58	12	3	64900	1.97	6	59
3900	1.69	16	3	22600	1.68	3	35
3000	1.34	7	3	68200	2.08	4	50

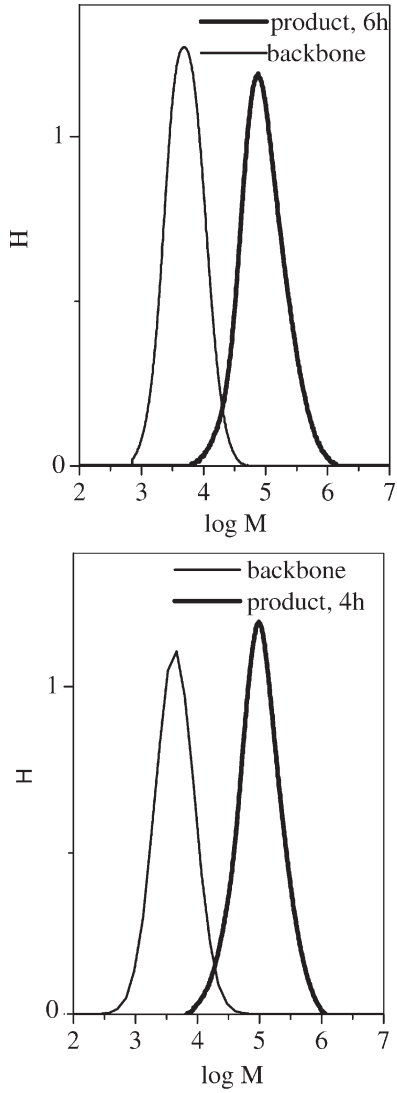

Figure 3.
Molecular weight distribution of the graft polymer (64900 g/mol) obtained from the Mas-BzEt-BIPNO-co-styrene prepolymer (4000 g/mol) after 6 h and of the graft polymer (68200 g/mol) obtained from the Mas-BzEt-BIPNO-co-styrene prepolymer (3000 g/mol) after 4 h (n-butylacrylate polymerization in bulk, 125 °C, 12 and 7 mmol/L styrene backbone).

The molecular weight distribution showed only one peak attributed to the graft product. The results demonstrate that the polymerization proceeded in a living manner.

Conclusion

The synthesis of graft polymers with different backbones and with styrene or n-butylacrylate as side chains is presented in this paper. In the first step prepolymers were prepared by the copolymerization of either Mas-BzEt-TEMPO with styrene, butylacrylate, methylmethacrylate and butylmethacrylate or Mas-BzEt-BIPNO with styrene under free radical conditions. In both cases no significant influence of the bulky substituent on the copolymerization

behaviour could be observed. In the following step prepolymers with TEMPO residues were employed as macroinitiators for the nitroxide mediated graft polymerization of styrene and prepolymers with BIPNO residues initiated the graft copolymerization of *n*-butylacrylate. All polymerizations were carried out in bulk at 125 °C. In the case of the graft polymerization of *n*-butylacrylate 5 mol% of BIPNO were added to the polymerization system with respect to the concentration of the initiating groups. The purified graft copolymers were characterized in detail with GPC. It could be established that graft polymerizations proceeded in a living manner when macroinitiators with molecular weights up to 10000 g/mol were used. The products obtained with *n*-butylacrylate showed a star-like shape.

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[1] E. Rizzardo, *Chem. Aust.* **1987**, *54*, 32.
[2] D. H. Solomon, E. Rizzardo, P. Cacioli, *US Patent* 4581429 **1986**, *Chem. Abstr.* **1985**, *102*, 221335q.
[3] D. H. Solomon, *J. Polym. Sci.,Part, A Polymer Chem.* **2005**, *43*, 5748.
[4] K. Matyjaszewski, *Chem. Eur. J.* **1999**, *5*, 3095.
[5] T. Pintauer, K. Matyjaszewski, *Coord. Chem. Rev.* **2005**, *249*, 1155.
[6] M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689.
[7] G. Moad, E. Rizzardo, San H. Thang, *Polymer* **2008**, *49*, 1079.
[8] K. A. Davis, K. Matyjaszewski, *Advances in Polym.Sci.* **2002**, *159*, 1, J. -F. Lutz, *Polym. Int.* **2006**, *55*, 979.
[9] C. J. Hawker, *Angew. Chem.* **1995**, *107*, 1623.
[10] H. Zhang, Z. Guo, J. Huang, *J. Polym. Sci. Part A: Polymer Chem.* **2002**, *40*, 4398.
[11] J. Nicolas, Ch. Dire, L. Mueller, J. Belleney, B. Charleux, *Macromolecules* **2006**, *9*, 8274.
[12] Y. Miura, Y. Isobe, T. Nakamura, M. Sugiura, Y. Okamoto, *Polym. Journal* **2005**, *37*, 617.
[13] M. Bothe, G. Schmidt-Naake, *Macromol. Rapid Comun.* **2003**, *24*, 609.
[14] S. Flakus, K. Mandel, M. Bartsch, G. Schmidt-Naake, *Macromol. Rapid Commun.* **2005**, *26*, 1698.

