Synthesis of functional polymers by atom transfer radical polymerization

*H. Malz, H. Komber, D. Voigt, I. Hopfe, J. Pionteck**

Institut für Polymerforschung Dresden e.V., Hohe Straße 6, D-01069 Dresden, Germany

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SUMMARY: The preparation of monochelic polystyrene by atom transfer radical polymerization (ATRP) was investigated. The polymer analogous pathway by substitution of the bromide by an alcoholate resulted in significant elimination of the bromide and the degree of functionalization was low. Better results were achieved by the use of functional initiators. Carboxylic acid- and anhydride-bearing initiators were prepared by bromination of the commercially available 4-ethylbenzoic acid and the 4-methylphthalic anhydride, respectively. With these two products monochelic polystyrenes were synthesized. Further modification of the 4-(1-bromoethyl)benzoic acid led to initiators with a hydroxy or an oxazoline moiety. Again, the respective functional polystyrenes were obtained.

Introduction

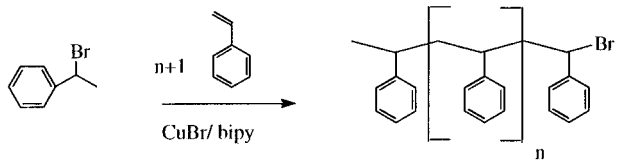
Polymer blends, mixtures of two polymers, often offer synergistic effects compared with the pure polymers such as better processibility, chemical resistance, and mechanical properties. However, most polymer pairs are immiscible. Without compatibilization, this leads to rough morphologies, poor phase adhesion and hence inferior mechanical properties. Thus, there is a great demand for additives to improve the compatibility of the polymer blends.

These additives can, for example, be block copolymers made of the two blend components. The block copolymer is then located at the interface between the immiscible blend phases. It reduces the interfacial tension and avoids coalescence of the dispersed phase. This results in a finer morphology and better phase adhesion thus improving the properties of the blend. However, when melt mixing a block copolymer into a polymer blend much of the compatibilizer does not migrate into the interface but is lost by micelle formation[1]. Due to the costs of block copolymers this can limit the process economically.

Another strategy to compatibilize a blend is the use of reactive polymers. Here the compatibilizing block copolymer is formed in-situ while preparing the blend. Micelle formation is thus impossible. Since the block copolymer formation takes place directly in the interphase it is much more efficient than the addition of premade additives. Thus, only 1.4 to 1.7% of block copolymer is sufficient to compatibilize a reactive blend system compared to 3 to 10% for a premade block copolymer[1]. Examples of reactive polymers for blend compatibilization can be found in ref.[2]

Block copolymers as well as reactive polymers for compatibilization of blends can be synthesized by "living" free radical polymerization. Among the different methods one of the most versatile mechanisms is the atom transfer radical polymerization (ATRP) reported by Matyjaszewski[3–7]. This method utilizes a halogenide as initiator as well as the copper (I) halogenide as catalyst and a 2,2′-bipyridine (bipy) as cocatalyst (Scheme 1).

Scheme 1: Atom transfer radical polymerization of styrene



With ATRP polymers and block copolymers with a low polydispersity of P_d = 1.05 can be yielded[8]. Thus, the formation of defined polystyrene-*block*-polymethacrylate copolymers, polystyrene-*block*-polymethacrylate-*block*-polystyrene) triblock copolymers, and random poly(styrene-*co*-methacrylate) was reported[7, 9]. Further, branched and hyperbranched polymers and copolymers could be synthesized[10].

As can be seen from Scheme 1 the product of an ATRP has a bromine atom at one chain end. This opens the possibility to functionalize the polymer further by nucleophilic substitution reactions. S_N reactions were used for the preparation of azido- and allyl functional polystyrene and acrylates[11, 12].

Another route to monochelic polymers in a one-pot synthesis by use of functional initiators was proposed by Matyjaszewski and Wang[7]. Haddleton et al.[13, 14] have reported the preparation of methyl methacrylate with a hydroxy- and a carboxylic acid end group. As initiators, 2-hydroxyethyl 2-bromo-2-methylpropionate and 2-bromo-2-methylpropionic acid were used.

Our objective was to synthesize and characterize monochelic polystyrene with a low polydispersity for

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later reactive blending applications. We used both the polymer analogous reaction route by S_N of the bromine and the one-pot synthesis by polymerization of styrene with a functionalized initiator. The reaction products were investigated with Fourier transform infrared spectroscopy (FTIR), ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, matrix assisted laser desorption ionization mass spectroscopy (MALDI TOF MS), and size exclusion chromatography (SEC).

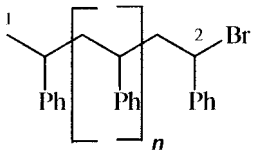
Experimental part

Materials

Copper(I) bromide, (1-bromoethyl)benzene, 4-hydroxybenzoic acid methyl ester, potassium fluoride, pyridine, thionyl chloride, methylene chloride, and ethanolamine were received from Aldrich. 2,2′-Bipyridine, 4-ethylbenzoic acid, 4-methylphthalic anhydride were purchased from Lancaster. *N*,*N*′-bis(trimethylsilyl)urea was received from Fluka.

Bromide-functional polystyrene[3] **(1)**

0.924 g (1-bromoethyl)benzene (5 mmol), 2.35 g 2,2′-bipyridine (15 mmol), and 0.728 g CuBr (5 mmol) were added to 52 g (0.5 mol) styrene. The solution was evaporated and flushed with nitrogen (5 ×) to remove oxygen. Subsequently, it was heated to 130 °C in an oil bath. After 20 min the polymerization was stopped by cooling in an ice bath. $\overline{M}_n$ = 2500 g/mol, P_d = 1.18.

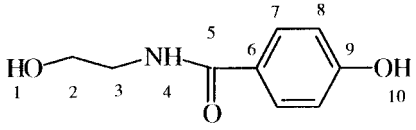


1

^{1}H NMR ($CDCl_3$ end-groups only): δ = 0.92–1.10 (H^1); 4.34–4.60 (H^2).

N-2-hydroxyethyl-4-hydroxybenzamide[15]

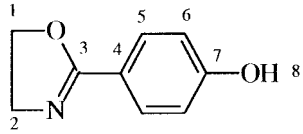
100 g 4-hydroxybenzoic acid methyl ester (0.65 mol) were mixed with 115 g ethanolamine (1.95 mol) and heated to 150 °C for 5 h. The generated methanol was removed by distillation. The excess ethanolamine was then removed by vacuum (<1 mbar). Subsequently, the reaction product was recrystallized in ethanol. Yield: 87 g (74% of theory), *m.p.*: 154 °C.



^{1}H NMR (DMSO-d_6): δ = 3.29 (q, H^3); 3.48 (t, H^2); 4.70 (br, H^1); 6.78 (d, H^8); 7.72 (d, H^7); 8.15 (t, H^4); 9.85 (br, H^{10}).

2-(4-Hydroxyphenyl)-1,3-oxazoline[15] (**2**)

50 g *N*-2-hydroxyethyl-4-hydroxybenzamide (0.276 mol) were suspended in 250 ml dichloromethane. To the vigorously stirred suspension 60.41 ml thionyl chloride (0.83 mol) were added slowly through an addition funnel at 0 °C. The suspension was subsequently stirred for 15 h at room temperature. After that, the product was filtered off and washed with methylene chloride. It was then carefully added to a vigorously stirred ice cooled sodium hydrocarbonate solution. The 2-(4-hydroxyphenyl)-1,3-oxazoline was then recrystallized in ethanol. Yield: 38.7 g (86%), *m.p.*: 195.5 °C.



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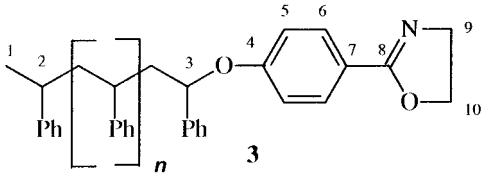
^{1}H NMR (DMSO-d_6): δ = 3.87 (t, H^2); 4.32 (t, H^1); 6.79 (d, H^6); 7.67 (d, H^5); 10.3 (br, H^8).

Williamson ether synthesis

1.0 g (0.3 mmol) bromine-terminated polystyrene was dissolved in 10 ml DMF. 0.25 g potassium carbonate and 0.3 g (1.8 mmol) 2-(4-hydroxyphenyl)-1,3-oxazoline were added. The reaction solution was heated to 80 °C and stirred for 15 h. Subsequently, the solution was precipitated into methanol. To remove the DMF the product was then taken into 10 ml THF and precipitated into methanol for a second time. The ^{1}H NMR shifts of the oxazoline end-group are concentration dependent. All data were obtained from concentrated solutions. The ^{1}H and ^{13}C NMR spectra were assigned by use different 2D-NMR techniques.



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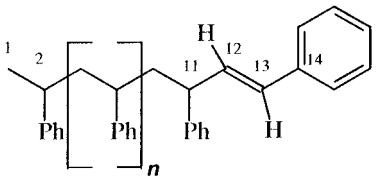

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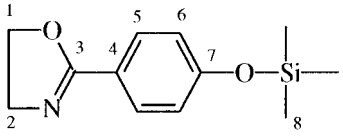
^{1}H NMR ($CDCl_3$; only end-group signals): δ = 0.98; 1.06 (H^1); 2.42 (H^2); 3.11 (H^{11}); 3.92 (H^9); 4.21 (H^{10}); 4.62, 4.81, 4.93 (H^3); 6.04–6.21 (H^{12}, H^{13}); 7.73 (H^6).

^{13}C NMR ($CDCl_3$; only end-group signals): δ = 20.9–21.4 and 23.0–23.7 (C^1); 36.74, 37.42 (C^2); 46.36 (C^{11}); 54.65 (C^9); 67.27 (C^{10}); 77.9–78.2 (C^3); 115.44 (C^5); 120.01 (C^7); 129.57 (C^6); 129.7–130.4 (C^{13}); 132.9–134.9 (C^{12}); 137.41, 137.48 (C^{14}); 160.2–160.7 (C^4); 164.32 (C^8).

2-(4-Trimethylsiloxyphenyl)-1,3-oxazoline[16]

4.0 g of powdered 2-(4-hydroxyphenyl)-1,3-oxazoline were suspended in 40 ml dichloromethane (dry, stored over molecular sieve). 2.52 g *N,N′*-bis(trimethylsilyl)urea were added and the mixture was heated for three hours under reflux. After that the solution was cooled to −18 °C over night to facilitate the precipitation of the formed urea. The urea was filtered off and the dichloromethane was removed by evaporation. The silyl ether was yielded as a cloudy liquid. Purification was performed in a sublimator at 75 °C under oil pump vacuum. The clean product condensed as white solid. *m.p.*: 55 °C.



^{1}H NMR ($CDCl_3$): δ = 0.27 (s, H^8); 4.03 (t, H^2); 4.40 (t, H^1); 6.84 (d, H^6); 7.85 (d, H^5).

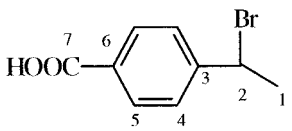
^{13}C NMR ($CDCl_3$): δ = 0.17 (C^8); 54.53 (C^2); 67.60 (C^1); 119.9 (C^6); 120.73 (C^4); 129.96 (C^5); 158.23 (C^7); 164.7 (C^3).

Ether synthesis (Sinhababu variation)[17]

0.5 g bromide-terminated polystyrene ($\overline{M}_n$ = 2500 g/mol), 0.4 g 2-(4-trimethylsiloxyphenyl)-1,3-oxazoline, and 0.1 g potassium fluoride were dissolved in 10 ml dry DMF (stored over molecular sieve). The solution was heated to 40 °C and stirred for 3 h under argon. Subsequently, the polystyrene was precipitated into methanol, redissolved in acetone, and again precipitated into methanol.

4-(1-Bromoethyl)benzoic acid[18] (**5**)

A mixture of 40 ml tetrachloromethane, 5.0 g 4-ethylbenzoic acid, 5.93 g *N*-bromosuccinimide (NBS), and 0.333 g benzoyl peroxide were heated under reflux. At 90 °C (oil bath temperature) the reaction started under foaming. The bath temperature was slowly increased to 100 °C over a time of 1 h. Subsequently, the reaction mixture was cooled in an ice bath and the product was filtered off. To remove the succinimide the filtrate was washed with 100 ml of water. After recrystallization in ethanol 3.0 g of a white crystalline powder were yielded. *m.p.*: 144 °C.



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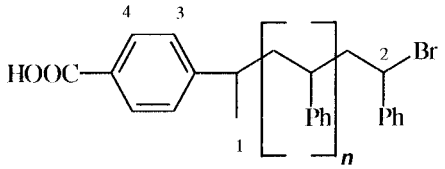
^{1}H NMR (DMSO-d_6): δ = 1.99 (d, H^1); 5.54 (q, H^2), 7.61 (d, H^4); 7.92 (d, H^5); 13.00 (br, H^7).

^{13}C NMR ($CDCl_3$): δ = 26.51 (C^1); 47.68 (C^2); 129.12 (C^6); 149.01 (C^3); 130.68 and 127.01 (C^4 and C^5); 171.43 (C^7).

Polymerization with 4-(1-bromoethyl)benzoic acid

200 mmol 2,2′-bipyridine, 50 mmol CuBr, and 50 mmol 4-(1-bromoethyl)benzoic acid were added to 2.2 mol of styrene. After degassing the solution was heated to 130 °C. The reaction product was precipitated into methanol. Molar masses are given in Tab. 1.



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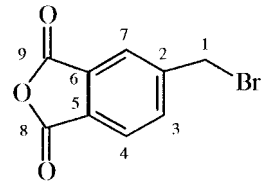
^{1}H NMR ($CDCl_3$; end groups only): δ = 0.92−1.12 (H^1); 4.34−4.60 (H^2); 7.89 (H^4).

4-(Bromomethyl)phthalic anhydride **(6)**

5.0 g 4-methylphthalic anhydride, 5.5 g *N*-bromosuccinimide, 0.31 g benzoyl peroxide, and 40 ml tetrachloromethane were heated under reflux. At 90 °C (oil bath temperature) the reaction started under foaming. The oil bath temperature was slowly increased to 100 °C over a time of 1 h. The reaction mixture was cooled in an ice bath, and the succinimide was filtered off. The filter cake was washed with 2 × 20 ml diethyl ether, and the organic phases were combined. Subsequent washing with 50 ml of cold water was executed to remove the succinimide. The aqueous phase was shaken out twice with 50 ml of diethyl ether and the organic phases were recombined. Concentration in the evaporator yielded 6.0 g of a yellowish oil (active bromine content 70% (^{1}H NMR)).



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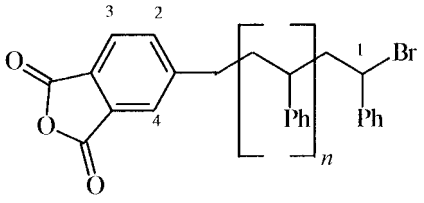
^{1}H NMR (DMSO-d_6): δ = 4.78 (s, H^1); 7.65 (d, H^3); 7.68 (d, H^4); 7.75 (s, H^7).

^{13}C NMR (DMSO-d_6): δ = 32.69 (C^1); 128.96, 129.07 and 131.43 (C^3, C^4, and C^7); 133.37 and 132.42 (C^5 and C^6); 141.02 (C^2); 168.20 and 168.28 (C^8 and C^9).

Polymerization with 4-(bromomethyl)phthalic anhydride

1.01 g 4-(bromomethyl)phthalic anhydride, 0.61 g CuBr, and 1.97 g 2,2′-bipyridine were added to the precalculated amount of styrene. The solution was evaporated and flushed with nitrogen (5 ×) to remove oxygen. Subsequently, the solution was heated to 130 °C. The reaction was stopped after 24 h. After dissolution of the solid polystyrene in toluene the CuBr was filtered off. Subsequently, the reaction

product was precipitated into heptane. Molar masses are given in Tab. 3.



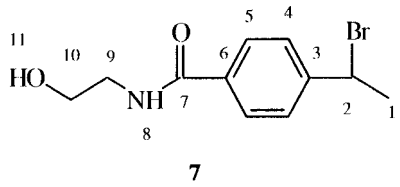
^{1}H NMR ($CDCl_3$; end groups): δ = 4.34–4.61 (H^1); 7.36 (H^2); 7.52 (H^4); 7.75 (H^3).

IR (cast film on KBr; anhydride group only): 1850 cm^{-1} and 1780 cm^{-1}; 1258 cm^{-1}.

N-(2-hydroxyethyl)-4-(1-bromoethyl)benzoic acid amide (**7**)

5.0 g 4-(1-bromoethyl)benzoic acid were suspended in dry toluene. The suspension was cooled to 0 °C and 4.55 g phosphorous pentachloride were added. The reaction proceeded for 15 h at room temperature. Subsequently, the solvent and the formed phosphorous oxide trichloride were removed at room temperature under vacuum. The residual oil was taken into 50 ml chloroform.

1.4 g ethanolamine (dry, over molecular sieve) and 2.25 g triethylamine were dissolved in 100 ml methylene chloride. The solution was cooled to −5 °C. After that, the acid chloride solution was added carefully within 1 h. Subsequently, the solution was stirred for another 2 h. The solution was washed with 50 ml water and the phases were separated. The aqueous phase was shaken out with 50 ml methylene chloride. Then, the organic phases were combined and dried over magnesium sulfate. After filtering off the drying agent the product was isolated by careful addition of petrol ether. 2.5 g white needles, m. p. 99 °C, were yielded.



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^{1}H NMR ($CDCl_3$): δ = 2.03 (d, H^1); 2.90 (br, H^{11}); 3.60 (q, H^9); 3.81 (t, H^{10}); 5.19 (q, H^2); 6.80 (br, H^8); 7.46 (d, H^4); 7.74 (d, H^5).

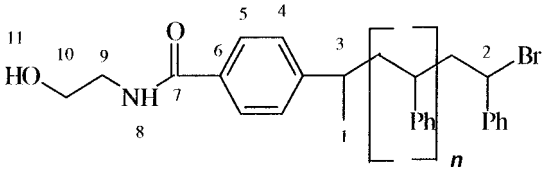
^{13}C NMR ($CDCl_3$): δ = 26.53 (C^1); 42.79 (C^9); 48.60 (C^2); 62.32 (C^{10}); 127.09 (C^4); 127.42 (C^5); 133.97 (C^6); 146.75 (C^3); 167.88 (C^7).

Hydroxy-terminated polystyrene

0.272 g *N*-(2-hydroxyethyl)-4-(1-bromoethyl)benzoic acid amide (**7**) (1 mmol), 0.15 g CuBr (1 mmol), and 0.477 g 2,2′-bipyridine were given into 50 ml styrene. The solution was freed of oxygen and then heated to 110 °C under argon atmosphere.

After 2 h the reaction was stopped by cooling with ice water. The copper bromide was removed by filtration. Afterwards, the polymer was precipitated into methanol, redissolved in acetone, and precipitated again.

$\overline{M}_n$ (GPC): 3500 g/mol; P_d = 1.3.



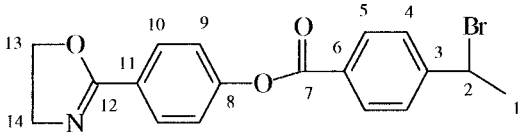
^{1}H NMR ($CDCl_3$; end groups only): δ = 0.92–1.10 (H^1); 2.39 (H^3); 3.63 (H^9); 3.84 (H^{10}); 4.36–4.60 (H^2); 7.52 –7.68 (H^5).

4-(1,3-Oxazoline-2-yl)phenyl-4-(1-bromoethyl)benzoate (**8**)

2.0 g 4-(1-bromoethyl)benzoic acid were suspended in dry toluene. The suspension was cooled to 0 °C and 1.82 g phosphorous pentachloride were added. The reaction proceeded for 15 h at room temperature. Subsequently, the solvent and the formed phosphorous oxide trichloride was removed at room temperature under vacuum. The residual oil was taken into 20 ml chloroform.

0.49 g potassium hydroxide, 1.41 g 2-(4-hydroxyphenyl)-1,3-oxazoline, and 0.25 g tetrabutylammonium chloride were dissolved in 20 ml water. The solution was cooled to 0 °C. Then the chloroform solution of the acyl chloride was added slowly under vigorous stirring. The reaction solution was stirred for another three hours under room temperature, then the phases were separated. The organic phase was washed with sodium hydrogen carbonate solution and distilled water. Then it was dried over magnesium sulfate. After filtering off the drying agent the chloroform solution was carefully diluted with petrol ether until the solution became cloudy.

After cooling in the fridge the product crystallized as a white powder. Yield 2.2 g (67%).



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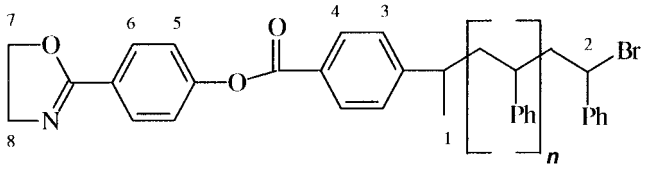
^{1}H NMR ($CDCl_3$): δ = 2.08 (d, H^1); 4.08 (t, H^{14}); 4.46 (t, H^{13}); 5.23 (q, H^2); 7.28 (d, H^9); 7.58 (d, H^4); 8.03 (d, H^{10}); 8.18 (d, H^5).

^{13}C NMR ($CDCl_3$): δ = 26.48 (C^1); 47.66 (C^2); 54.92 (C^{14}); 67.76 (C^{13}); 121.66 (C^9); 125.50 (C^{11}); 127.12 (C^4); 129.02 (C^6); 129.64 (C^{10}); 130.67 (C^5); 148.93 (C^3); 153.16 (C^8); 163.92 (C^{12}); 164.18 (C^7).

Oxazoline-functional polystyrene

0.375 g 4-(1,3-oxazoline-2-yl)phenyl 4-(1-bromoethyl)benzoate (1 mmol) were dissolved in 50 ml styrene. To the solu-

tion 0.15 g CuBr and 0.477 g 2,2′-bipyridine were added. The solution was evacuated five times and subsequently flushed with argon to remove oxygen. Then it was heated to 110 °C. After two hours the polymerization was stopped by cooling in ice water. Yield: 2.5 g. $\bar{M}_n$ (GPC) = 2400 g/mol; P_d (GPC) = 1.31.



^{1}H NMR($CDCl_3$): δ = 1.08–1.24 (H^1); 4.20 (H^8); 4.56 (H^7); 4.65 (H^2); 7.11 (H^5); 7.44 (H^3); 8.11 (H^6); 8.25 (H^4).

Fourier transform infrared spectroscopy (FTIR)

Measurements were executed on an IFS 66 (Bruker). The resolution was 2 cm^{-1}. Samples were either solvent cast on a KBr disc from THF or investigated as KBr pellet. Temperature dependent FTIR was executed with a variable temperature cell (P/N 21.500; Specac). The heating rate was 10 °C/min.

MALDI-TOF MS

The experiments were performed on a HP G2030A MALDI TOF MS system (Hewlett Packard). The desorption/ionisation was induced by a pulsed N_2 laser. The mass spectra were obtained by 28 kV acceleration voltage. The matrix for measurements of polystyrene was 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) modified by Ag/trifluoroacetic acid. The mixture of sample and matrix was dried on the sample holder under vacuum. The measurements were carried out by linear mode and positive polarity.

Size exclusion chromatography (SEC)

The SEC measurements were performed with a modular chromatographic equipment containing a refractive index detector at ambient temperature. A single column Hibar PS 40 (Merck) was used. The injection volume was 20 µl. The sample concentration was c = 2 g/l. The flow rate was 1 ml/min. The coupling experiments were carried out at room temperature with chloroform as eluent. The molecular weights were calculated by use of a PS calibration, determined with polystyrene standards (KNAUER).

NMR spectroscopy

The NMR spectra were obtained on a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C. $CDCl_3$ and DMSO-d_6, respectively, were used as solvent, lock, and internal standard ($CDCl_3$: $\delta(^1H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.00 ppm; DMSO-d_6: $\delta(^1H)$ = 2.50 ppm, $\delta(^{13}C)$ = 39.60 ppm). Signal assignments given in this paper were verified by ^{1}H-^{1}H shift correlated (COSY) spectra, ^{1}H-^{13}C heteronuclear multiple quantum correlation (HMQC) experiments, and ^{1}H-^{13}C heteronuclear multiple bond correlation (HMBC) experiments. The puls sequences included in the Bruker software package were used.

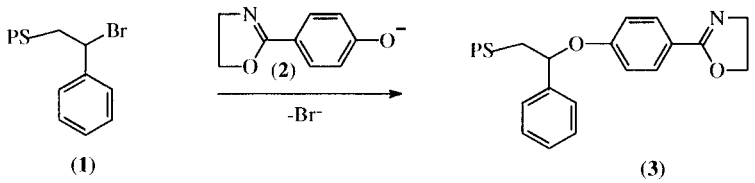
Results

Polymer analogous reactions

As can be seen from Scheme 1, the product of an ATRP of styrene with (1-bromoethyl)benzene as initiator is a bromide-terminated polymer **1**. Thus, the nucleophilic substitution (S_N) of the bromine at the chain end is the most obvious possibility to synthesize monochelic polystyrenes from **1**. For this polymer analogous reaction it would be of advantage to find one general method that could be used to introduce a variety of functional groups.

Alcohols are a common functional group in organic chemistry and thus alcohols with an additional reactive moiety group are readily available. They form ether bonds in an S_N reaction, which is chemically and thermally resistant. Therefore, it seems advantageous to substitute the bromine by an alcoholate. This so called Williamson ether synthesis is a well known reaction which proceeds via an S_N2 pathway. To test the strategy of a general reaction, 2-(4-hydroxyphenyl)-1,3-oxazoline was employed in the attempt to introduce an oxazoline group at the polystyrene end (Scheme 2). The aromatic alcohol was chosen since phenolates are easier to access than aliphatic alcoholates due to their acidic character. Product of the reaction is an aryl alkyl ether **3**. To simplify the analysis of the products a low molecular weight polystyrene **1** with a molar mass of $\bar{M}_n$ = 2500 g/mol was synthesized following the method of Wang and Matyjaszewski[3]. Fig. 1 shows the ^{1}H NMR spectrum of **1**. The signals at 4.34–4.60 ppm are due to the bromide end group of polystyrene. The signals at 0.92–1.10 ppm indicate the

Scheme 2: Williamson ether synthesis



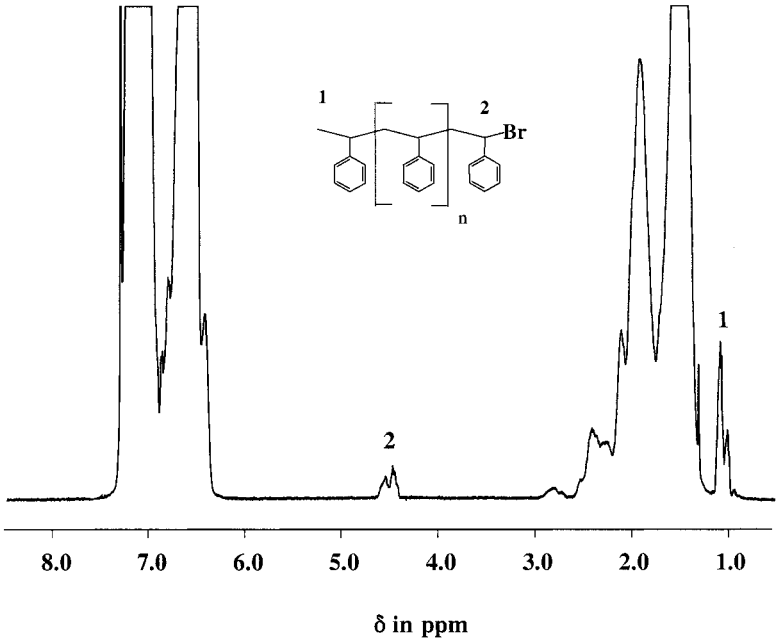


Fig. 1. ^{1}H NMR spectrum of bromine-terminated polystyrene

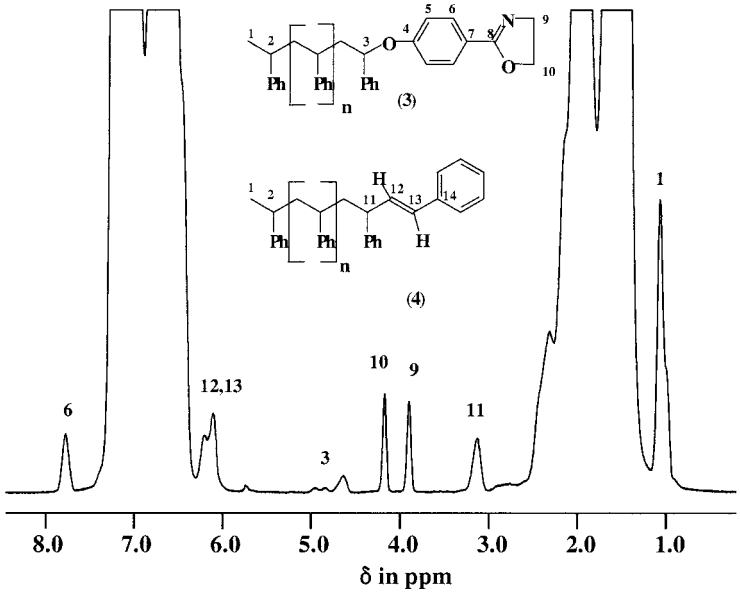


Fig. 2. ^{1}H NMR spectrum of the conversion product of the Williamson ether synthesis

methyl group of the initiator residue. The synthesis was performed in DMF at 80 °C with potassium carbonate as base. Fig. 2 shows the ^{1}H NMR spectrum of the reaction product. By comparison with Fig. 1 it can be seen that the broad signal at 4.34–4.60 ppm vanished. Thus, the bromide reacted completely. Instead, new signals can be observed. The signals at 3.92 ppm, 4.21 ppm, and 7.73 ppm are due to the desired phenyl oxazoline moiety at the polystyrene end. However, elimination took place as well. This is indicated by the olefinic signals of a vinyl-terminated polystyrene at 6.04–6.21 ppm. The structures of both, the oxazoline-functional polystyrene **3** and the elimination product **4** were established by combination of 1D and 2D NMR methods. ^{1}H and ^{13}C NMR signal assignments for both end groups are given in the Experimental part. By integration of the ^{1}H NMR end-group resonances it became clear that the elimination and not the S_N reaction was the predominant reaction pathway. The yield of the desired oxazoline functional polystyrene **3** was calculated to be only 30%. It should be

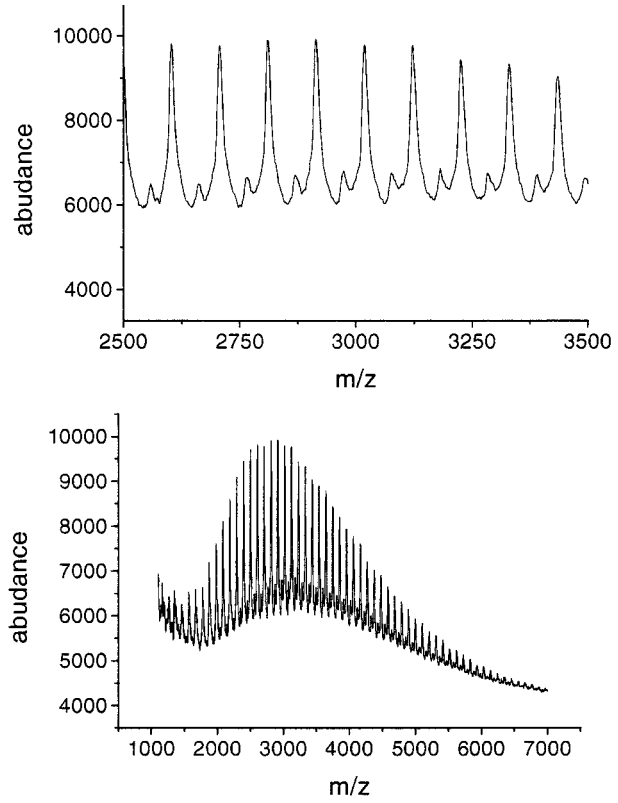


Fig. 3. MALDI TOF MS of the conversion product of the Williamson ether synthesis. The large signal distribution indicates the elimination product **4**. The small signal distribution belongs to the oxazoline-terminated PS **3**

mentioned that the ^{1}H NMR shifts and the signal shapes for the oxazoline group are very sensitive to the concentration of the solution, obviously due to association and solvation effects.

The reaction product was further investigated by MALDI TOF MS. The interpretation of the spectrum was facilitated by the fact that the initiator residue in the polymer has the mass of a styrene unit +1 (see Scheme 1). The spectrum (Fig. 3) shows two different

$$\frac{m_A}{z} = (x+1)\cdot M_{styrene} + M_{Ag^+} \quad (1)$$

$$\frac{m_B}{z} = (x+2)\cdot M_{styrene} + M_{Ag^+} + 59 \quad (2)$$

distributions. The *m*/*z* values for the series of the large signals can be expressed by Eq. 1. The variable *x* is the degree of polymerization. The molar mass of Ag^+ has to be added since the chains are desorbed as Ag^+ adducts. This is in agreement with the structure of **4**, vinyl-terminated polystyrene.

The *m*/*z* values for the series of the small signals follows Eq. 2. The mass of 59 can be explained by the mass difference of the hydroxyphenyl end group (163 g/mol) and a styrene unit (104 g/mol).

The difference of the signal intensities of the two distributions is not in accordance with the NMR results, which proposed an elimination of 70% of the bromides. This can be caused by a preferred desorption of **4** from the matrix, erroneously indicating an even higher extent of elimination.

To increase the yield of the oxazoline-functional polystyrene the reaction was repeated at various temperatures and with potassium hydroxide as base. Still, substantial elimination took place. The use of pyridine as soluble base failed to show any effect.

At last, to avoid the use of a base altogether a reaction pathway suggested by Sinhababu et al.[17] was tried. The 2-(4-hydroxyphenyl)-1,3-oxazoline was first transferred into its trimethylsilyl ether. Then the substitution of the bromide was executed in a DMF solution at 40 °C with potassium fluoride as catalyst. However, again elimination led to the major product. Therefore, the polymer analogous functionalization of the polystyrene was abandoned. However, it shall be mentioned that the product of the elimination, vinyl-terminated polystyrene **4** itself, might be an interesting starting material for further reactions such as epoxidation or hydrosilylation. Finally, the use as macromonomer could be considered as well.

Functional polystyrenes by use of functional initiators

The modification of monochelic polymers suffers from many drawbacks. The concentration of reactive groups is very low. This complicates a complete conversion. In addition, as could be seen above, side reactions can become predominant leading to poor yields of the desired product. And once two polymers with different functional groups are formed next to each other, it is almost impossible to separate the mixture since the chemical effect of the end group is negligible compared to the large polymer backbone.

Therefore, the direct introduction of a functionality into a polymer by a modified initiator seems to be favorable. If it can be excluded that no polymer chains are formed by chain transfer reactions it can be assumed that all macromolecules bear the desired chemical functionality. And, in addition, non-reacting impurities in the initiator can be removed easily from the polymer matrix.

A corresponding structure to the (1-bromoethyl)benzene initiator used by Wang and Matyjaszewski is the 4-(1-bromoethyl)benzoic acid (**5**). This compound can easily be prepared from the commercially available 4-ethylbenzoic acid by a radical bromination reaction with *N*-bromosuccinimide[18]. The polymerization of styrene with this initiator could be performed in the same way as with (1-bromoethyl)benzene. ^{1}H NMR data verifying the synthesis of carboxylic acid terminated polystyrene are presented in the Experimental part. Tab. 1 shows molar

Tab. 1. Carboxylic acid-terminated PS

Sample	$\overline{M}_n$/(g/mol)	$\overline{M}_w$/(g/mol)	$\overline{M}_w/\overline{M}_n$
1	8800	10900	1.24
2	12500	15400	1.23
3	15000	18700	1.25
4	16900	21900	1.30

masses of different polystyrenes that were polymerized with **5**.

When measuring low molecular weight carboxylic acid terminated polystyrene by GPC uncharacteristic high polydispersities were found. This led to the assumption that the carboxylic acid end group shows an end-group effect in the GPC analysis. Therefore, ^{1}H NMR spectroscopy and MALDI TOF MS measurements were conducted. The molar masses determined by these three different techniques are summarized in Tab. 2. It can be seen that the molar masses of the low molecular weight polystyrenes were underestimated by the size exclusion technique. In addition, the polydispersities were overestimated. Enthalpic effects can be presumed responsible for this phenomenon which will be subject of further investigations.

The carboxylic acid group can be used for reactions with a variety of other functionalities such as the hydroxyl, amine, carbodiimide, epoxide, and oxazoline groups[2]. Thus, a large variety of polymers can be blended with the carboxy-terminated polystyrene. To investigate the processes occurring during reactive blending FTIR-spectroscopy is frequently applied[19]. Therefore, we were interested in the IR absorptions of the aromatic carboxylic acid. Usually carboxylic acids are found in the associated form in hydrophobic solvents, as which the polystyrene matrix can be considered. However, with end-functionalized polystyrene the concentration of the carboxylic acid is very low and the mobility is hindered due to the large polymer backbone. This influence could be seen when investigating two polystyrenes with a number average molar mass of 4900 g/mol and a number average molar mass of 15000 g/mol, respectively, by means of FTIR spectroscopy. Free aromatic carboxylic acids absorb at 1730 cm^{-1} while the associated aromatic carboxylic acids show a characteristic band at 1688 cm^{-1}. Therefore, changes in the ratio of these two bands give direct information about an alteration of the association

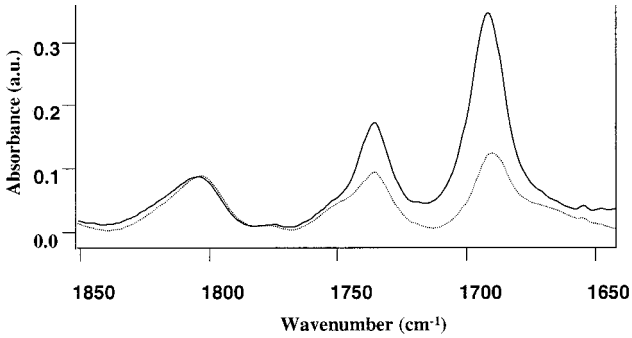


Fig. 4. Dependence of the molar mass on the degree of association of carboxylic acid end groups. The solid line shows the absorption of a PS with $\overline{M}_n$ = 4900 g/mol, the dashed line shows the absorption of a PS with $\overline{M}_n$ = 15000 g/mol

state of the carboxylic acid groups. As can be seen in Fig. 4, with an increase in molar mass the ratio between the free and the associated carboxylic acid groups changed towards the free carboxylic acids. But reactive blending is performed at high temperatures. Therefore, a solution-cast film of the carboxylic acid-terminated polystyrene with $\overline{M}_n$ = 15000 g/mol was heated up to 230 °C. Again, the change in the association behavior of the carboxylic acids could be observed. The free acid band increased significantly while the associated acid band vanished completely (Fig. 5). When cooling down to room temperature, the effect was reversed. However, the starting point was not reached even after two days. This suggests that the diffusion hindrance in the polymer matrix, especially below the glass temperature, blocks the association of the free carboxylic acid groups.

Another interesting functionality for reactive blending is the anhydride group. Reaction with amines leads to the formation of the stable imide bond. Therefore, in analogy with the preparation of **5**, 4-methylphthalic anhydride was brominated with *N*-bromosuccinimide to yield 4-(bromomethyl)phthalic anhydride (**6**). The yield of the reaction was about 70%. Further purification of the reaction product proved difficult due to the reactivity of the anhydride group. But since the 4-methylphthalic anhydride does not interact during polymerization it proved more favorable to calculate an active bromine concentration of the initiator and to remove the unconverted methylphthalic acid after the polymerization of styrene. Again, with **6** as initiator styrene could be polymerized

Tab. 2. Molar masses and polydispersities of carboxylic acid terminated PS determined by different methods

No.	$\overline{M}_n$(GPC)/g/mol	P_d (GPC)	$\overline{M}_n$(^{1}H NMR)/g/mol	$\overline{M}_n$(MALDI TOF MS)/g/mol	P_d (MALDI TOF MS)
1	1200	1.61	3700	3500	1.08
2	2000	1.62	4900	4500	1.08
3	2200	1.57	5300	4900	1.07

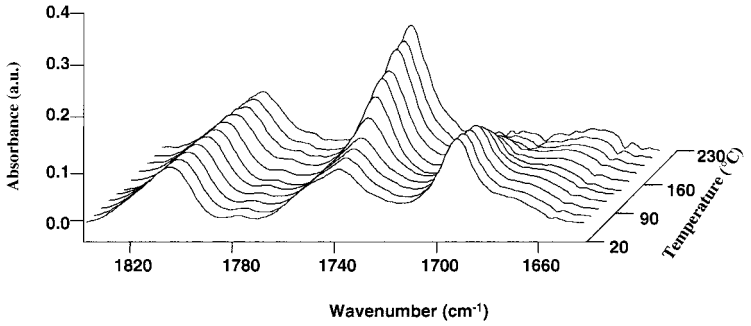


Fig. 5. Dependence of the degree of association of carboxylic acid end groups on the temperature. Investigations were carried out on a PS with $\overline{M}_n$ = 15000 g/mol

Tab. 3. Anhydride terminated PS

Sample	$\overline{M}_n$/(g/mol)	$\overline{M}_w$/(g/mol)	$\overline{M}_w/\overline{M}_n$
1	7100	9300	1.31
2	10000	14300	1.43
3	12000	17000	1.42

by applying the standard procedure. However, to avoid the formation of methyl esters, the polystyrene was precipitated into heptane instead of methanol. Tab. 3 shows the molecular weights and polydispersities of three different anhydride terminated polystyrenes. The high polydispersities are not typical for an atom transfer radical polymerization. However, taking into account the possibility of partial hydrolysis of the anhydride group, this observation can be explained by the different elution behavior of the anhydride-terminated polystyrene compared to the phthalic acid functional polystyrene. This could be concluded from the GPC curves. While sample 1 (Tab. 3) displayed the expected narrow distribution, the peaks of samples 2 and 3 showed a shoulder at shorter residence times.

By modification of initiators bearing a reactive moiety further functionalities can be provided for the ATRP of styrene. Thus, the transformation of **5** by reaction with phosphorous pentachloride leads to the formation of a reactive carboxylic acid chloride which can be coupled to a variety of functional groups. The reaction with ethanolamine yielded **7** in high purity. It resembles nothing but an initiator with an aliphatic alcohol group. Alcohols can react with carboxylic acids, isocyanates, and epoxides, functional groups which play an important role in polymer chemistry. Again, **7** was used to polymerize styrene according to the standard procedure. The ^{1}H NMR assignments for the characteristic end groups of a low molecular weight PS are given in the Experimental part. The structure of the *N*-(2-hydroxyethyl)benzoic acid amide and bromide end groups was established by 2 D NMR techniques.

Finally, coupling of the carboxylic acid chloride of **5** with 2-(4-hydroxyphenyl)-1,3- oxazoline yielded the oxazoline-functional initiator **8**. It was used to prepare the desired oxazoline-functional polystyrene, which was not obtained by the polymer analogous reaction. Again, the standard procedure for an ATRP could be applied. However, to avoid a reaction of the benzylic bromine with the oxazoline end group[20] the polymerization was performed at 110 °C instead of 130 °C which still guaranties a sufficient conversion. Fig. 6 shows the ^{1}H NMR spectrum of the oxazoline-functional polystyrene. The signals at 4.56 ppm and 4.20 ppm are due to the oxazoline ring while the signal at 1.08–1.24 ppm is due to the methyl group of the initiator. As can be seen by comparison with Fig. 2, no elimination took place. The signal of the bromide end group overlaps with a signal of the oxazoline ring, but can be identified by the broad base of this resonance. Its chemical shift is 4.65 ppm. The structure was established unambiguously by 2D NMR techniques.

Conclusions

Atom transfer radical polymerization of styrene was applied to synthesize end-functional polymers needed for reactive blend applications. The attempt to use the Williamson ether synthesis in order to introduce different functional groups by an S_N reaction lead to insufficient yields of only 30% due to the occurrence of elimination of the bromide. Attempts to optimize the reaction by use of different bases and eventually by use of a potassium fluoride catalyzed reaction did not succeed.

Therefore, the use of functional initiators proved to be the method of choice. The functional bromides could be readily synthesized by a bromination reaction with *N*-bromosuccinimide. Two exemplary initiators were prepared, 4-(bromomethyl)phthalic anhydride and 4-(1-bromoethyl)benzoic acid. Further functionalization of the 4-(1-bromoethyl)benzoic acid lead to a hydroxy- and an oxazoline-functional initiator. However, the synthesis of additional initiators containing different reactive moieties

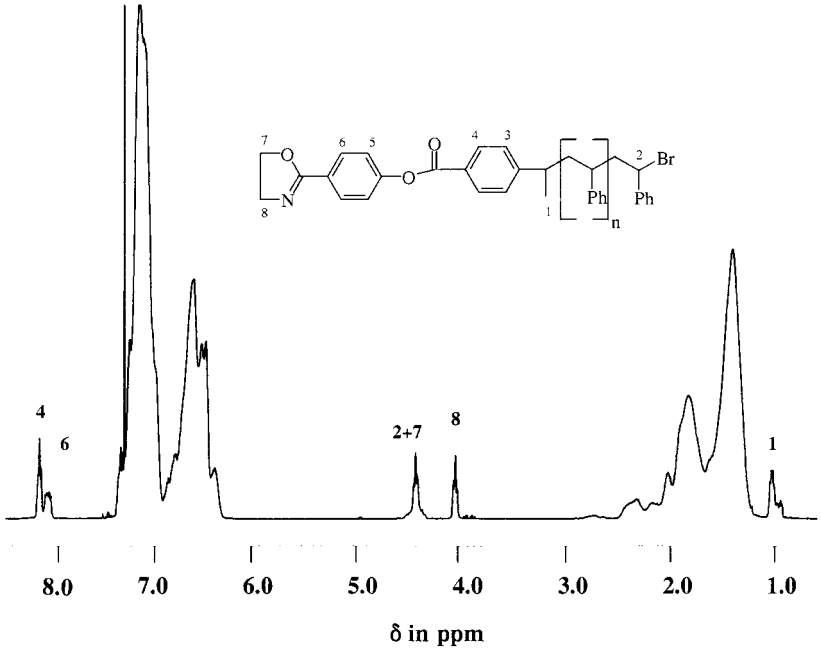


Fig. 6. ^{1}H NMR spectrum of oxazoline-terminated polystyrene

such as aromatic hydroxy groups by the bromination reaction can be imagined, as well.

The aforementioned initiators were used to prepare monochelic polystyrene of different molar masses. The analysis of end-functional polymers revealed that the end group, although low in concentration, has an influence on the polymer character. Thus, the molar mass of carboxylic acid terminated low molecular weight polystyrene determined by GPC differed significantly from the molar masses determined by ^{1}H NMR spectroscopy and MALDI TOF MS. On the other hand, the polymer backbone itself has an influence on the properties of the end-group. Although carboxylic acid moieties tend to associate in hydrophobic media, a long polystyrene chain can hinder this tendency. Thus, with increase in molar mass the ratio between associated and free acids changes towards the free acids.

By use of functional initiators, carboxy-, anhydride-, hydroxy-, and oxazoline-functional polystyrenes were made available. A large variety of reactions can be performed with these groups. With the monochelic polymers our research will now focus on the preparation of reactive blends.

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