Synthesis and Characterization of α,ω-Macrozwitterionic Block Copolymers of Styrene and Isoprene

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ABSTRACT: The synthesis of a novel type of telechelic block copolymer is described: bifunctional poly(styrene-*b*-isoprene) diblock copolymers were prepared by anionic polymerization using [2-[(*N*,*N*-dimethylamino)methyl]phenyl]lithium as the initiator and 1,3-propanesultone as the terminating reagent. Quaternization of the tertiary amino group yields the α,ω-macrozwitterionic block copolymer. The applicability of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) for end group analysis is demonstrated. Using analogous bifunctional polystyrene samples, MALDI-TOF-MS enabled us to identify side reactions reducing end functionality in previous synthetic routes to macrozwitterions. The conversion of chain ends further checked by conventional methods such as dye extraction and titration is found to be almost quantitative.

Introduction

Block copolymers and ionomers are materials with unique physical properties which have been studied by extensive experimental and theoretical work in the last two decades.[1−3] These heterogeneous polymer systems exhibit a rich equilibrium phase behavior, giving rise to a large variety of microdomain structures.

Block copolymers easily form spherical, cylindrical or lamellar morphologies in the microphase-separated state at sufficiently low temperatures.[4] In these ordered phases which can be controlled through the copolymer molecular weight and composition, periodicity of the microstructure is on a length scale of several nanometers. The properties of ionomers are largely governed by ionic aggregates being surrounded by an unpolar polymer matrix. As an example, for polyisoprene (PI) end-functionalized with the highly polar sulfobetaine group, the formation of a body-centered-cubic lattice with long-range order was evidenced by SAXS.[5] Although a detailed description of the ionic aggregates is still missing, it is generally accepted that ion pairs associate to form so-called multiplets, i.e. quadruplets, sextuplets, etc.[6,7] Similarities in the phase behavior of block copolymers and ionomers were recently highlighted by Nyrkova *et al.*, showing that ionomer multiplets correspond to microdomains of strongly segregated diblock copolymers with short A blocks in the superstrong segregation regime.[8] Apparently, there is a strong analogy in the self-assembling processes in multiphase polymer systems, notwithstanding the nature of the interaction governing the behavior.

In the present study we describe the synthesis and characterization of an α,ω-macrozwitterionic block copolymer. In this case chain-end interactions *and* block segregation are expected to control the phase behavior. Furthermore, due to the Coulomb attraction of chain ends attached to unlike blocks, segregation of like block segments will partially be inhibited. For low molecular weights microphase separation is likely to be dominated by chain end association. Very recently, Pispas *et al.* described the synthesis and dilute solution properties of styrene−isoprene block copolymers with sulfobetaine end groups on one and both sides of the linear chain.[9,10] In this case, however, ionic and block segregation do *not* necessarily oppose each other. On the other hand, block copolymers bearing oppositely charged chain ends constitute a "frustrated" polymer system, a new concept which is expected to give rise to interesting phase and dynamic behavior.

The synthesis of macrozwitterions has attracted synthetic chemists for about 20 years.[11,12] Antonietti *et al.* were the first who described the synthesis of a polystyrene macrozwitterion: By means of the anionic polymerization technique, using [2-[(*N*,*N*-dimethylamino)methyl]phenyl]lithium as the initiator and 1,3-propanesultone as the terminating reagent, a bifunctional polystyrene was obtained which could be quaternized and converted into the α,ω-macrozwitterion by ultrafiltration.[13,14] Herein, we use the same initiating and terminating system for the preparation of the end-functionalized styrene−isoprene diblock copolymers. Since quantitative conversion of the chain ends is essential for further investigations end functionality is then carefully checked by advanced analytical tools. In this way side reactions in the previous synthetic route are identified and an improved approach to macrozwitterions is developed.

End group analysis has always been of central importance in the characterization of telechelic polymers.[15] Traditional methods such as NMR, IR, UV−vis, elemental analysis, or titration techniques only allow indirect quantification by measuring the concentration of chemical subunits. Care has to be taken, for instance, that low molecular weight impurities are quantitatively removed. Here we employ MALDI-TOF-MS (**m**atrix-**a**ssisted **l**aser **d**esorption/**i**onization **t**ime-**o**f-**f**light **m**ass **s**pectrometry)[16−19] for end group analysis along with traditional methods. Using MALDI-TOF-MS, individual, mass-resolved polymer chains can be identified within a molecular weight distribution, though not all polymers are suitable for this technique. Up to ca. 10 000 g/mol polymer masses can be determined very precisely (with an error of less than 1 Dalton), making MALDI-TOF-MS highly attractive for end group analysis.

Experimental Section

Reagents. Pure and carefully dried solvents and monomers were used; all steps for further purification of the chemicals were performed under nitrogen.

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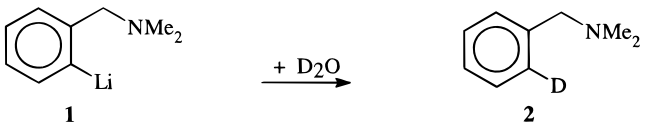
Benzene (Aldrich), cyclohexane (Janssen Chimica), tetrahydropyran (THP, Aldrich), and diethyl ether (Riedel-de Haën) were refluxed over potassium; isoprene (Fluka) and styrene (Riedel-de Haën) were mixed with *n*-BuLi (1.6 mol/dm^3 Janssen Chimica) and 9-fluorenyllithium, respectively, and distilled under reduced pressure just before use. 1,1-Diphenylethene (DPE, Aldrich) was distilled under reduced pressure after stirring with *n*-BuLi, which results in the formation of the red 1,1-diphenylhexyl anion. *N*,*N*-Dimethylbenzylamine (DMB, Aldrich) and 1,3-propanesultone (Aldrich) were purified by refluxing over CaH_2 and distilling before use.

Synthesis of the Initiator. The synthesis of the functional initiator was carried out at room temperature under nitrogen. Freshly distilled DMB (2.0 g, 14.8 mmol) was dissolved in a freshly prepared mixture of 10 mL of diethyl ether and 40 mL of cyclohexane. A *s*-BuLi solution (11.4 mL of a 1.3 M solution in hexane, 14.8 mmol) was then added and the solution allowed to stand for 18 h. Under these conditions *N*,*N*-dimethylbenzylamine is converted into **1** (Figure 1) by metalation.

The resulting white precipitate was filtered off, washed with cyclohexane, and dissolved in THP. This solution can be stored under nitrogen at −20 °C for months without decomposition of the initiator. Characterization: (a) 300 MHz ^{1}H-NMR (THF-d_8) δ = 2.15 (s, 6H), 3.50 (s, 2H), 6.77 (m, 3H), 7.98 (m, 1H); (b) reaction of the white solid with D_2O yields a colorless liquid (**2**) according to the following scheme:



1 **2**

IR spectrum of **2**: ν_1 = 733 cm^{-1} and ν_2 = 777 cm^{-1}, indicating ortho substitution.[20] The effective concentration of the initiator $n_{\text{initiator}}$ was determined from the stoichiometric ratio

$$n_{\text{initiator}}\ (\text{mol}) = m_{\text{mon}}\ (\text{g})/M_{\text{n pol}}\ (\text{g/mol})$$

where m_{mon} is the mass of the reacted monomer and $M_{\text{n pol}}$ the molar mass of the resulting PS as determined by size exclusion chromatography (SEC, see below).

Preparation of the α,ω-macrozwitterionic block copolymers. The polymerization was carried out under nitrogen at room temperature. Block copolymers of styrene and isoprene were obtained by sequential addition of the monomers (Figure 1). In a typical run styrene was mixed with the ca. 15-fold volume of a 70/30 (v/v) benzene/diethyl ether mixture. The calculated amount of the initiator was then added via syringe and the solution shaken vigorously (a). In order to obtain a fraction of the styrene prepolymer, a small amount of the solution was removed after 30 min and quenched with degassed methanol. To the remaining part was then added the calculated amount of isoprene in order to obtain a 50/50 vol % PS−PI block copolymer. The yellow solution was then allowed to stand for 2 h (b). The basicity of the isoprenyl anion was subsequently reduced by adding a 5-fold excess of DPE (c). Non-sulfonated polymers, as needed for SEC, were obtained by quenching small amounts of the solution with degassed methanol.

Since the yield of the synthesis was greater than 99%, the volume composition of the block copolymer could be calculated from the ratio of the added monomers together with the densities of 1.05 and 0.9 g/cm^3 for PS and PI, respectively. Although this is not a direct measure of the molecular weight, our experience together with that of other groups[21] on PS-*b*-PI copolymers shows that the synthesis stoichiometry provides the most quantitative measure of M_n, rather than postpolymerization characterization methods, such as light scattering or osmometry. In order to show this, the PI content was separately checked by a combination of SEC on the PS precursor and ^{1}H-NMR on the block copolymer (see the following section).

Termination of the living chain ends was achieved by carefully titrating the anions from red to colorless with a 0.5% solution of 1,3-propanesultone in benzene at room temperature (d). All samples were precipitated in methanol (addition of small amounts of LiCl for low molecular weights) and dried under vacuum.

Separation of the bifunctional polymers from small amounts of the unsulfonated species in the scale of several grams was achieved by HPLC using a reversed-phase column (RP 18, Lichrosphere, 5 μm, Merck) and a methanol/THF solvent gradient.[22] The pure amine-capped, sulfonated diblock was then quaternized with methyl bromide in a 75/25 (v/v) THF/nitromethane solution[14] (e).

End Group Analysis. The efficiency of the initiation and termination reaction was checked by analyzing the chain-end functionality of the anionically prepared samples.

(1) Amino Group: The functionality of the amino chain ends was checked by MALDI-TOF-MS using PS chains initiated by the initiator **1** and quenched with methanol. In addition, titration of the amine-capped PS and PS-*b*-PI was performed with 5 mM HCl (in 90/10 (v/v) THF/MeOH) and bromphenol blue as indicator. Before titration, the polymers were precipitated two to three times in methanol to make sure that all free amine was removed.

(2) Sulfonate Group: Attempts to find suitable matrices or comatrices for MALDI-TOF-MS using PI or PS-*b*-PI for end group analysis failed. Since the living chain end determines the reactivity of the macroanions, not the polymer backbone, we circumvented this problem by using telechelic PS. To this end PS chains were end-functionalized in *exactly* the same way as the telechelic PS-*b*-PI copolymers: The styryl anions were reacted with DPE, just as the isoprenyl anions were reacted with DPE in the case of the block. Therefore, in both cases it is the same deep red macroanion formed by the DPE which reacts with the 1,3-propanesultone. Quantitative analysis of sulfonate end functionality was performed by following the dye-extraction[14] technique first described by Moeller *et al.*[23]

Instrumentation. SEC was performed using a Waters Model 590 pump and a UV detector (254 nm) in series with 10 μ-SDV gel columns having a porosity of 10^3, 10^5, and 10^6 Å. THF with a flow rate of 1 mL/min at 25 °C was used as the elution solvent. Molecular weight calculation was achieved by narrow standard calibration using PS standards. The microstructure of the PI units was analyzed by ^{1}H-NMR spectroscopy (Bruker AC300 instrument) in $CDCl_3$ at room temperature.

The MALDI-TOF measurements were performed with a Bruker Reflex mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm (LSI N_2 laser, 10^6−10^7 W/cm^2, 100 μm spot diameter). The instrument can be used in linear and reflectron mode. All measurements shown in this paper were recorded in the reflectron mode. The detector consists of a dual microchannel plate for analysis of polymers below 15 000 Dalton. The matrices for all experiments were 1,8,9-trihydroxyanthracene and 5-chlorosalicylic acid (both Aldrich). Samples were prepared by dissolving the polymer in THF at a concentration of 10^{-4} mol/L. A 10 μL aliquot of this solution was added to 10 μL of a 0.1 mmol/mL matrix solution, dissolved in THF. For the detection of positive ions 1 μL of a solution of 5 mg of silver trifluoroacetate (Aldrich) in 1 mL of THF as the cationization reagent was added to the matrix/analyte solution. A 1 μL aliquot of the mixture was applied to the multistage target and air dried. The ions were accelerated by a potential of 33.65 kV and reflected by 35 kV. In the case of the detection of positive ions only silver-cationized $(M-Ag)^+$ species were detected, whereas negative ions were formed by loss of lithium from the end group $(M-SO_3)^-$. Polystyrene (M_n = 6000 g/mol) was used for an external calibration, immediately before measurement. The mass inaccuracy determined in this way is about 0.05%.

Results and Discussion

The α,ω-macrozwitterionic block copolymers were synthesized by anionic polymerization using [2-[(*N*,*N*-dimethylamino)methyl]phenyl]lithium (**1**, DMB−Li) as the initiator and 1,3-propanesultone as the terminating reagent. The reaction scheme is depicted in Figure 1.

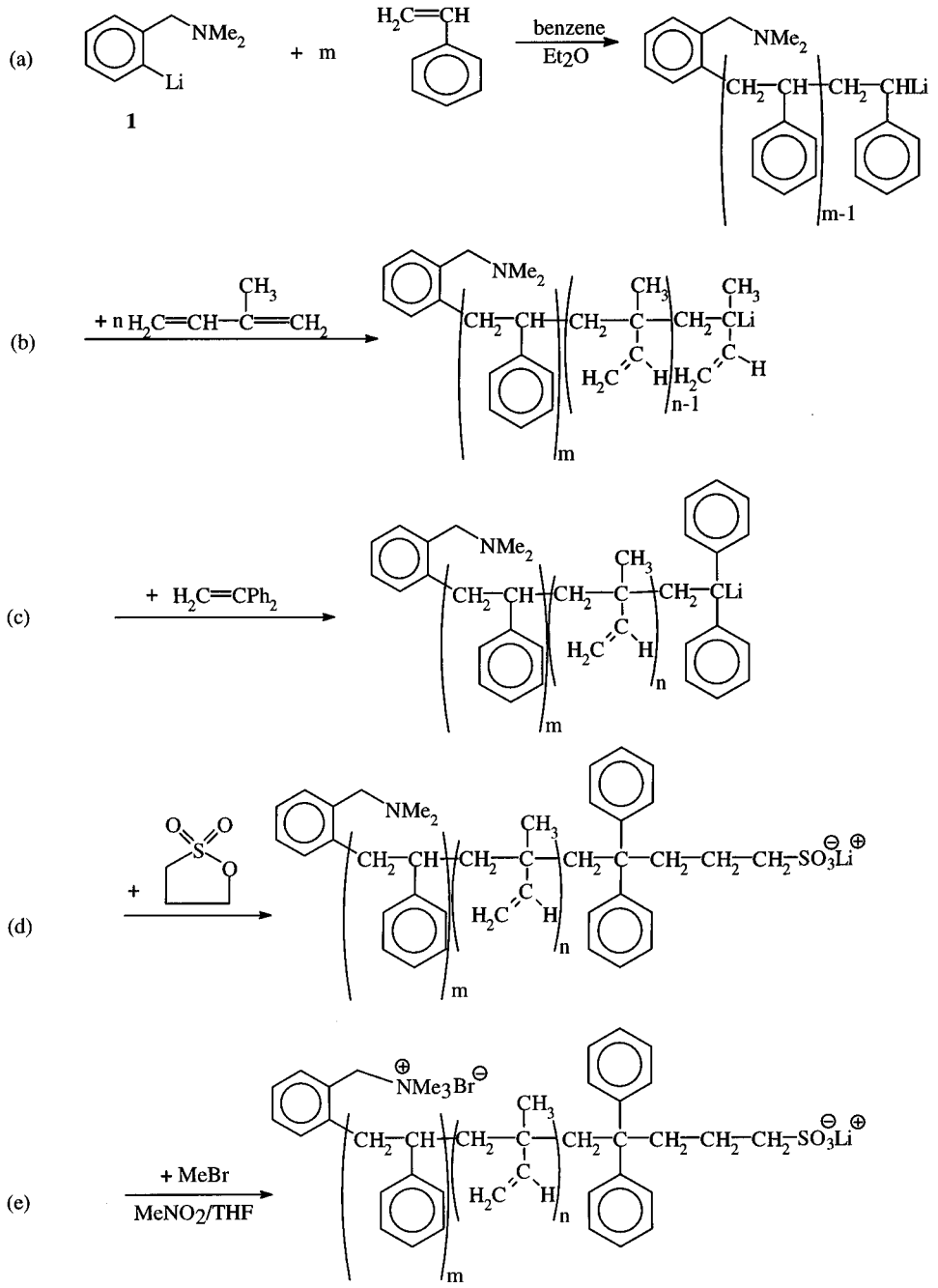


Figure 1. Reaction scheme for the synthesis of an α,ω-macrozwitterionic block copolymer of styrene and isoprene.

After subsequent polymerization of the different monomers (steps a and b in Figure 1), the resulting block copolymer is quenched with DPE (step c), and termination of the resulting anions is achieved by adding 1,3-propanesultone (step d). For quaternization of the amine-capped, sulfonated diblocks, methyl bromide is used as the reagent (step e).

In the following, the crucial steps in the synthesis of α,ω-macrozwitterionic block copolymers with quantitative chain-end functionality, namely the initiation, termination, and quaternization reaction, are described separately. In each section results of the MALDI-TOF-mass spectrometry and other analytical tools are presented in order to monitor the reaction paths.

(1) Initiation Reaction. To check the degree of functionality using **1** as the initiator, polystyrene samples of low molecular weights were prepared by following the procedure first described by Antonietti *et al.*[13] This method involves *in-situ* preparation of **1** in an Et_2O/toluene mixture. MALDI-TOF-MS allows us to detect individual molecular weights accurately enough to determine the mass of the end groups. The mass spectrum of the resulting polymer is shown in Figure 2a.

There are two series of equidistant mass peaks, indicating that different end groups are attached to the polystyrene. The ions detected in each series should have *m*/*z* values corresponding to *n* styrene repeating units (104.15 Dalton, Da), a silver atom (ionization cation, 108 Da), and both end groups. Since termination was achieved by quenching with methanol, i.e. protonation (1 H = 1 Da), the molecular weight of the initiator simply is:

$$(m/z)_{\text{initiator}} = (m/z)_{\text{detected ion}} - (n104.15 + 108 + 1)$$

For the two series of equidistant mass peaks centered around 2300 and 3000 Da the result for $(m/z)_{\text{initiator}}$ is

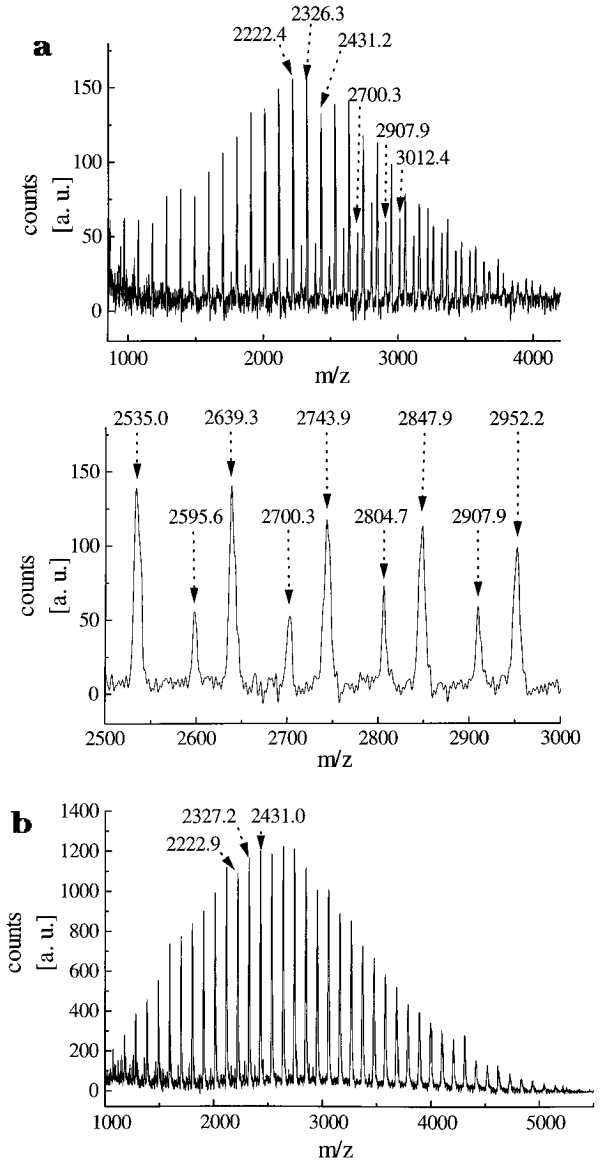


Figure 2. MALDI-TOF-mass spectra of polystyrene: (a) initiated by **1** following the *in-situ* preparation of the anionic initiator; (b) initiated by the isolated functional initiator **1**. In the bottom of Figure 2a the region between 2500 and 3000 *m*/*z* is depicted separately for clarity. Termination of the chain ends was achieved by protonation using degassed methanol; both spectra were recorded using 5-chlorosalicylic acid as the matrix and silver trifluoroacetate as the cationizing reagent. In case (a) chains are partially initiated by benzyl anions, while in (b) the pure amine-capped polymer is obtained.

135 and 91, respectively. The main series of mass peaks centered around 2300 Da can therefore be assigned to polystyrene (PS) initiated by **1** (135 Da). It appears that in the given solvent system the benzyl anion (91 Da), which is formed via deprotonation of toluene by *s*-BuLi or **1**, partially initiates polymerization. In order to achieve quantitative functionalization the synthetic procedure was subsequently modified as described in the Experimental Section.

The mass spectrum of a PS sample prepared in this way and quenched with methanol is depicted in Figure 2b. Comparison with Figure 2a reveals that only one series of equidistant mass peaks is detected which can be assigned to PS initiated by **1**. Thus, according to MALDI-TOF-MS a significantly higher degree of end functionalization is obtained compared to the previous procedure. In order to further quantify the effect,

Table 1. Molecular Weights M_n, Dispersity Index D, and Degree of End Functionalization f As Measured by Titration for Different Polystyrene Samples Initiated with DMB−Li (1)

sample	M_n (g/mol)[c]	$D = M_w/M_n$[c]	f (%)
DMB−PS[a]	2 000	1.17	81
DMB−PS[a]	14 700	1.07	68
DMB−PS[a]	37 000	1.03	74
DMB−PS[b]	2 400	1.16	98
DMB−PS[b]	4 800	1.07	100
DMB−PS[b]	10 200	1.07	104

[a] According to the synthetic route described in ref 13. [b] According to the new route. [c] Obtained by SEC.

amine-capped PS samples synthesized via the previous and new procedure were titrated with HCl. The results are summarized in Table 1 together with the characterization data for the different polymers obtained by SEC. In accord with the MALDI-TOF spectra (Figure 2) for the new route quantitative functionalization is indicated by titration whereas for the previous synthetic route about 20−30% of the chains do not carry the amino group.

For **1** to be an efficient starter for living anionic polymerization it is critical that the initiating step is fast compared to the propagation. M_w/M_n values < 1.1 were only obtained in the presence of an aliphatic ether, as described in ref 13.

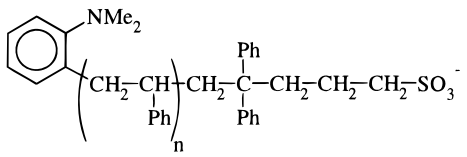
(2) Termination Reaction. In the case of the isoprenyl anion, the reaction with 1,3-propanesultone is largely dominated by proton transfer, which results in unfunctionalized chains. Sulfonation can be achieved, however, by introducing a 1,1-diphenylethene (DPE) unit at the living chain end. As pointed out in the Experimental Section, the efficiency of this quenching step was monitored by MALDI-TOF-MS using end-functionalized PS samples. Note that the living polystyryl anion was reacted with DPE in order to have the *same* living chain end, as in the case of the block copolymer (see Figure 1).

The MALDI-TOF-mass spectrum of a sample where styrene was initiated with **1** and the living anions were quenched successively with DPE and an excess of 1,3-propanesultone as described in previous works[12−14] is shown in Figure 3a.

As in the case of the initiation reaction, two series of equidistant mass peaks appear. Thus, the PS exhibits two different end functionalities. Since the spectra were recorded using negative polarity (anions), the molar mass of the end group due to the termination step can be obtained as follows:

$$(m/z)_{\text{end group}} = (m/z)_{\text{detected ion}} - (n104.15 + 135)$$

where 135 is the mass of the *N*,*N*-dimethylbenzylamine. For the more intense series with the maximum at 3352.8 Da the result for $(m/z)_{\text{end group}}$ is 302 Da, which is exactly the mass of 1 DPE (180 Da) plus the sulfonate group (122 Da) according to formula **3**:



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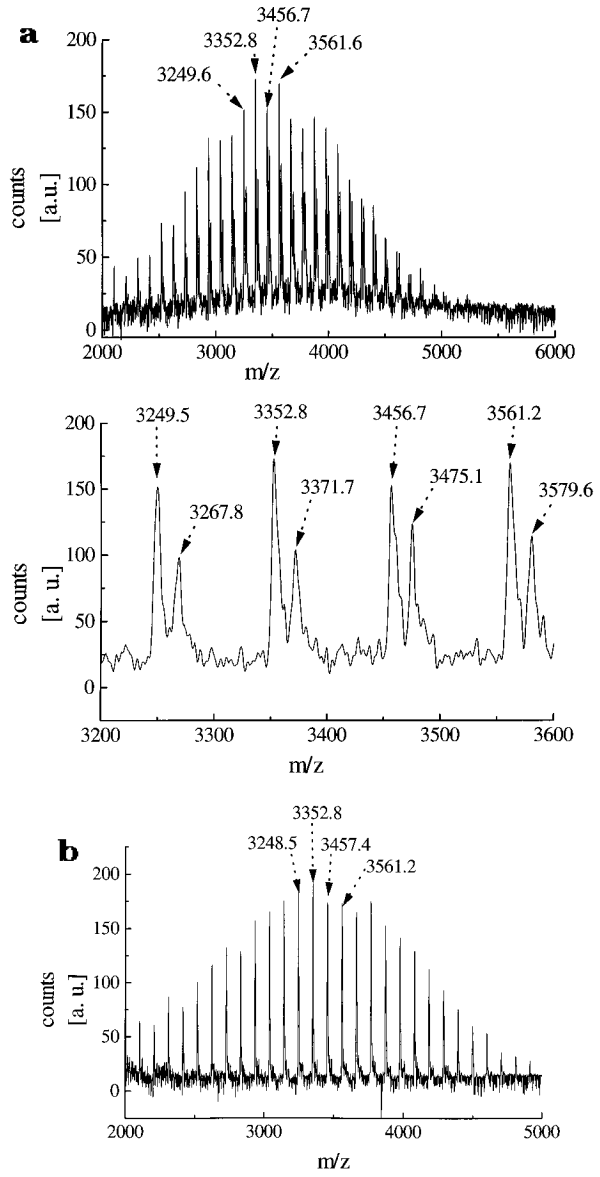
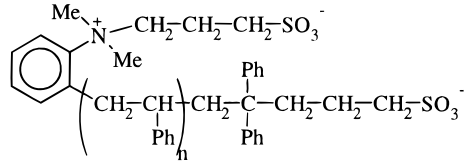


Figure 3. MALDI-TOF-mass spectra of polystyrene initiated by **1**, reacted with one DPE unit and terminated with (a) an excess of 1,3-propanesultone and (b) stoichiometric amounts of the sultone. In the bottom of Figure 3a the region between 3200 and 3600 *m/z* is depicted separately for clarity. 1,8,9-Trihydroxyanthracene was used as the matrix; only anions were recorded in both spectra; no salt was added. In case (a) **3** and the quaternary side product **4** occur, whereas in case (b) the pure bifunctional polymer is obtained.

The second series is shifted by 122 Da with respect to the first, which corresponds to the mass of the 1,3-propanesultone. Since cyclic sultones quaternize tertiary amines,[24] this second series can be assigned to the following species **4**:



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In fact, quaternization of tertiary amines using cyclic sultones has been applied recently by Pispas *et al.* to obtain sulfobetaine end groups from amine-capped block copolymers.[9] In order to avoid formation of the sulfobetaine, stoichiometric amounts of the 1,3-propanesultone were subsequently used in the synthesis. The MALDI-TOF-mass spectrum of the polymer obtained by carefully titrating the anions with 1,3-propanesultone from red to colorless is shown in Figure 3b. In contrast to Figure 3a there is only *one* series of mass peaks that corresponds to the bifunctional species **3**. Therefore, it can be concluded that *no* quaternization has occurred under these conditions. The same result is obtained when the degree of end functionalization is further checked and quantified by dye extraction following the procedure described by Heyne.[14] As expected, the bifunctional polystyrenes show an almost quantitative end group conversion (not shown here).

Next, α,ω-functionalized PS-*b*-PI copolymers were synthesized using the improved synthetic routes described above. In Table 2 the analytical results on the microstructure of the PI block together with results on the block copolymer molecular weights and compositions are presented. Due to the presence of THP and the tertiary amino group of the initiator, a 1,4-content below 30% was found for all PI blocks. The experimentally determined PI vol % is in excellent agreement with the synthesis stoichiometry. Note the excellent dispersity index of the block copolymers. While an almost quantitative end group conversion was found for the bifunctional polystyrenes the degree of sulfonate end functionality for the copolymers is of the order of 70%, as obtained by dye extraction. Most likely, the reason is that the isoprenyl anion does not react quantitatively with DPE (step c in Figure 1). However, removing the non-sulfonated copolymer by reversed-phase HPLC (see Experimental Section) yields pure bifunctional styrene-*b*-isoprene copolymers, as shown by the data in Table 2.

(3) Quaternization. The α-amino-ω-sulfonato polymers were quaternized with methyl bromide in a 75/25 (v/v) THF/nitromethane mixture. The resulting macrozwitterionic species could not be detected in a time-of-flight spectrometer, as expected for molecules with net zero charge. In the same way, attempts to use cationizing reagents failed.

Since quaternization only involves the tertiary amine group, not the sulfonate, the efficiency of this step was proved by quaternizing polystyrene which was initiated by **1** and quenched with degassed methanol. The MALDI-TOF-mass spectrum of the resulting sample is shown in Figure 4. Calculating the mass of the end group (145 Da) shows that the detected polymer uniformly carries the benzyltrimethylammonium group. Note that the same spectrum was obtained when silver was used as a cationizing reagent; i.e. unreacted amine-capped PS could not be found. This further supports that quaternization is quantitative.

In addition, we checked the degree of sulfonate end functionality before and after methylation by dye extraction and MALDI-TOF-MS using PS initiated by **1** and then successively treated with DPE and 1,3-propanesultone. It was found that under the experimental conditions described above no methylation of the sulfonate end group occurs.

Conclusion

In the present work, a novel type of telechelic polymer, i.e., an α,ω-macrozwitterionic block copolymer of

Table 2. Characterization of Amine-Capped, Sulfonated PS-*b*-PI Copolymers and the Corresponding PS Precursors

sample	M_n (g/mol) (PS block)[a]	$D = M_w/M_n$ (PS block)[a]	PI content (vol %)[b]	1,4-PI content (%)[b,c]	M_n (g/mol) (PS-*b*-PI)[a,b]	$D = M_w/M_n$ (PS-*b*-PI)[a]	$f_{sulfonate}$ (%)[d]
DMB−PS-*b*-PI-S	5 900	1.15	49	27	11 000	1.13	
DMB−PS-*b*-PI-S	12 700	1.07	50	29	24 000	1.09	>95
DMB−PS-*b*-PI-S	25 000	1.06	52	28	49 000	1.08	

[a] Obtained by SEC. [b] Obtained by ^{1}H-NMR. [c] With respect to total PI content. [d] Obtained by dye extraction on samples purified by HPLC.

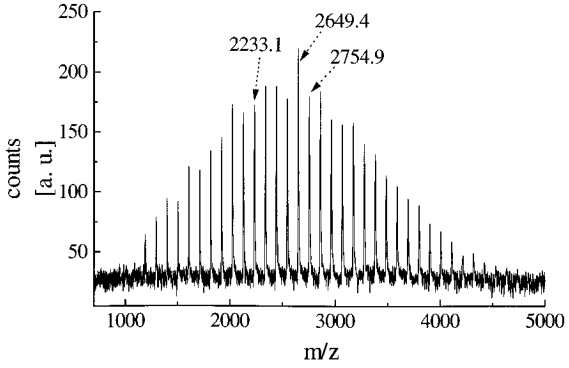

Figure 4. MALDI-TOF-mass spectrum of polystyrene initiated by **1**, quenched with methanol, and quaternized with methyl bromide. The spectrum was recorded without cationizing reagent using 1,8,9-trihydroxyanthracene as the matrix. Note that the same polymer was used for the quaternization as the one described in section 1; this is why the resulting MALDI-TOF-mass spectrum is similar to that in Figure 2b.

styrene and isoprene has been synthesized and characterized. It has been demonstrated how advanced analytical tools now available for the precise characterization of polymers can be employed to determine chain-end functionality in these systems. For the physical properties of these materials end functionality is expected to be a crucial parameter governing the observed behavior and should thus be controlled in a quantitative way. In the present case chain-end functionality has been carefully checked using MALDI-TOF-MS and side products arising in previous pathways have been identified. The synthetic routes have subsequently been improved. Most important, a new approach toward a stable initiator solution of [2-[(*N*,*N*-dimethylamino)methyl]phenyl]lithium has been developed. This solution can conveniently be stored for months and should also be applicable to other functional polymers in anionic polymerization as polydienes.

The improved synthetic route leads to a functionality of the tetraalkylammonium and the sulfonate end group which is very close to 1, respectively, as evidenced by a combination of different analytical tools.

The obtained α,ω-macrozwitterionic block copolymers, which constitute a "frustrated" polymer system, are expected to give rise to interesting phase and dynamic behavior. Experimental work to study the properties of these materials in solution and in the bulk are now in progress in our laboratory.

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References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(2) Pineri, M., Eisenberg, A., Ed. *Structure and Properties of Ionomers*; NATO ASI Series 198; D. Reidel Publishing Co.: Dordrecht, Holland, 1987.
(3) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic Press: New York, 1977.
(4) Herman, D. S.; Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1987**, *20*, 2940.
(5) Shen, Y.; Satinya, C. R.; Fetters, L.; Adam, M.; Witten, T.; Hadjichristidis, N. *Phys. Rev. A* **1991**, *43*, 1886.
(6) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
(7) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(8) Nyrkova, I. A.; Khokhlov, A. R.; Doi, M. *Macromolecules* **1993**, *26*, 3601.
(9) Pispas, S.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 1891.
(10) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1994**, *27*, 6307.
(11) Völkel, T.; Zweifel, H. *Makromol. Chem.* **1973**, *170*, 141.
(12) Eisenbach, C. D.; Schnecko, H.; Kern, W. *Makromol. Chem.* **1975**, *176*, 1587.
(13) Antonietti, M.; Heyne, J.; Sillescu, H. *Makromol. Chem.* **1991**, *192*, 3021.
(14) Heyne, J., Ph.D. Thesis, Universität Mainz, **1991**.
(15) Goethals, E. J., Ed. *Telechelic Polymers: Synthesis and Characterization*; CRC Press: Boca Raton, FL, 1989.
(16) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299.
(17) Karas, M.; Hillenkamp, F. In *Advances in Mass Spectrometry*; Longevialle, P., Ed.; Heyden & Son: London, 1989.
(18) Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F.; Giessmann, U. *Anal. Chem.* **1991**, *63/24*, 1193A.
(19) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi; F. *Macromolecules* **1995**, *28*, 4562.
(20) Jones, F. N.; Zinn, M. F.; Hauser, C. R. *J. Org. Chem.* **1963**, *28*, 664.
(21) See e.g.: Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922. Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.
(22) Schädler, V. Diploma Thesis, Universität Mainz, 1995.
(23) Moeller, M.; Mühleisen, E.; Omeis, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 213.
(24) Houben, J.; Weyl, T. *Methoden der organischen Chemie 11/2*; Thieme: Leipzig, 1958; p 593.

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