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International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

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Online publication date: 27 October 2010

To cite this Article Ji, Haining, Nonidez, William K. and Mays, Jimmy W. (2002) 'Side Reactions in Chain-End Sulfonated Polystyrene via Thin Layer Chromatography Coupled with Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry', *International Journal of Polymer Analysis and Characterization*, 7: 1, 181 – 194

To link to this Article: DOI: 10.1080/10236660214601

URL: <http://dx.doi.org/10.1080/10236660214601>

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Side Reactions in Chain-End Sulfonated Polystyrene via Thin Layer Chromatography Coupled with Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

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The specificity of the chain-end sulfonation reaction of polystyrene was studied by matrix-assisted laser desorption ionization/time-of-flight mass spectrometry (MALDI-TOF MS) after the products were separated according to their different end groups using thin-layer chromatography (TLC). By-products not previously reported are identified, and the side reactions that produce these by-products are discussed.

Keywords: TLC-MALDI; Side reactions; End-sulfonation; Functionalization; Anionic polymerization

Polymeric materials containing a desired functional group at one or both chain ends have practical and potential applications in a number of areas [1–3]. For some applications, such as reactive pre-polymers that were used to build block copolymers, graft copolymers or polymers with network architecture, it is important that only one unit of the functional groups of interest is placed at one or both of the polymer chain ends. It is also often desirable that the polymers have narrow molecular weight distributions

Received 25 August 2000; accepted 5 February 2001.

We sincerely thank the U.S. Army Research Office (ARO) for funding the purchase of the MALDI-TOF MS unit through its DURIP program (DAAG55-97-1-0075).

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and predictable molecular weights for better control of the properties of the resulting materials.

The living anionic polymerization technique is particularly suitable for the synthesis of chain-end functionalized polymers. This polymerization process minimizes chain termination and transfer reactions, allowing the preparation of polymers having rather uniform chain lengths^[4]. The stable anionic polymer chain end that remains after consumption of all the monomer is readily reacted with a variety of electrophilic reagents to yield the desired functional group at the terminal (ω) chain end^[5,6]. With the development of di- and tri-functional initiators, it is also possible to generate α,ω -difunctionalized (i.e., telechelic) polymers and end-functionalized star polymers^[7]. It is also possible to use a functional initiator to synthesize polymers with functional groups of the same or different types at both ends^[8]. It is generally necessary to use protecting groups in these initiators because most functional groups of interest are not stable in the presence of the anionic initiator or the growing chain ends. An alternative procedure is to terminate the living polymer chain with a reactive group (for example, a diene group), and the desired functional group may then be introduced by conducting functionalization reactions under much less critical conditions^[9].

Many of the established routes for the synthesis of chain-end functionalized polymers are not free from side reactions and rarely are they quantitative^[10,11]. However, information regarding the nature of these side reactions and the chemical structures of the by-products is often missing in the literature due to difficulties in characterization of the products.

End-group analysis is of central importance in the characterization of these materials. Traditional techniques such as nuclear magnetic resonance spectroscopy, infrared spectroscopy, ultraviolet-visible spectroscopy, elemental analysis or titration methods allow only indirect quantification by measuring the concentration of chemical subunits^[12]. Complete removal of the impurities is extremely important in applying these techniques, but this is difficult to achieve. With the development of matrix-assisted laser desorption ionization/time-of-flight mass spectrometry (MALDI-TOF MS), a technique that measures absolute molecular weight of individual polymer chains, accurate determination of the different chemical structures of end functional groups becomes possible^[13].

Inevitably, MALDI-TOF MS has some limitations. Polymers having a polydispersity index greater than 1.1 are difficult to reliably characterize by MALDI-TOF MS alone^[14]. In the past few years, on-line and off-line coupling of MALDI-TOF MS with size exclusion chromatography (SEC) has been reported^[15-17]. This coupling allows reliable SEC characterization of polymers with broad molecular weight distributions where suitable standards for SEC calibration are not available. As to complex polymers that are distributed in more than one direction of heterogeneity (block copolymers, end-functionalized polymers, stars,

cycles, dendrimers, etc.), SEC separation is generally difficult because these heterogeneities strongly superimpose and influence the molecular weight separation. Interaction chromatography (IC) is frequently employed in these cases. When critical or near critical conditions (controlled by either solvent composition or temperature) are used in such separations, polymers are separated according to the difference in their chemical structure such as end group, or composition of block copolymers^[18,19], rather than their molecular weights. Since the sample size required by MALDI is extremely small, thin-layer chromatography (TLC) can be an inexpensive, simple and fast alternative to IC for separating polymers according to their chemical structures^[20–22].

Our laboratory has recently embarked upon a mass spectroscopic study of chain-end functionalized polymers that were synthesized in-house under widely varied conditions in order to determine the specificity of these synthetic schemes and identify the significant by-products. Chain-end sulfonation of polystyrene is the subject of the current article. Quirk and Kim^[23] established a synthetic scheme for obtaining end-sulfonated polymer quantitatively. They suggested that attenuating the reactivity of the anionic chain-ends of poly(styryl)lithium by adding ethylene oxide or 1,1-diphenyl ethylene (DPE) before the reaction with sultone substantially increased the control of the reaction and under appropriate conditions yielded quantitative, or near quantitative, chain-end sulfonated polystyrene. In this article, we report the analysis of such materials using a combination of TLC and MALDI-TOF MS.

EXPERIMENTAL

Materials

The matrix material for MALDI, *trans, trans*-1,4-diphenyl-1,3-butadiene, and cationization agent, silver trifluoroacetate [Ag(TFA)], were purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin) and were used as received. Tetrahydrofuran (THF) from Fisher Scientific (Fair Lawn, New Jersey) was used as the common solvent in all the MALDI experiments. It was used as received. The materials for anionic polymerization—styrene, ethylene oxide, DPE, 1,3-propanesultone, *sec*-butyl chloride, lithium metal powder and benzene—were also purchased from Aldrich Chemical Co.

Synthesis

All reactions were carried out in all-glass sealed reactors, using standard high-vacuum techniques^[24,25]. Anionic polymerization of styrene using *sec*-butyl lithium was carried out in benzene at 25°C for 24 h. A

sample of living poly(styryl)lithium solution was removed from the reactor by heat sealing, terminated with degassed methanol and used as a reference polymer. The remainder of the solution was reacted first with 3-fold excess of ethylene oxide. A portion was then terminated with degassed methanol after 24 h and the remainder reacted with a 4-fold excess of 1,3-propanesultone. This solution was stored in a 40°C water bath for 4 days before it was precipitated in a 10-fold excess of a 1% HCl/methanol (v/v) solution. In another synthesis, the same procedure as above was carried out except a 4-fold excess of DPE was used in the place of the 3-fold excess of ethylene oxide. A volume of 1 mL THF, which was distilled over K/Na alloys and stored under vacuum in sealed glassware, was added before the introduction of DPE.

Thin Layer Chromatography

TLC plates (200 μm , 50/p, with fluorescent indicator F-254) purchased from Scientific Absorbents Inc. (Atlanta, Georgia) were employed to purify the products for MALDI-TOF MS analysis. Toluene was used as the developing solvent. The polymers were dissolved in toluene to make 5% solutions. Plates were intentionally overloaded in order to exaggerate the signal from products present in very small amounts. The polymers were then scraped from the developed TLC plate along with the silica gel. A volume of 100 μL THF was added to extract the polymers.

Sample Preparation for MALDI-TOF MS Analysis

A 20 mg/mL solution of *trans, trans*-1, 4-diphenyl-1,3-butadiene and 5 mg/mL solution of Ag(TFA) was prepared in THF. In the cases of the proton-terminated and hydroxyl-terminated polymers, a 10 μL volume of the matrix solution was mixed with 2 μL of the polymer solution and 1 μL of the Ag(TFA) solution. A volume of 0.5 μL of the above mixture was then spotted on the MALDI sample plate and air-dried before analysis. The sulfonated PS was treated as above except without addition of the Ag(TFA) solution.

Instrumental

The Voyager Elite MALDI-TOF MS from PE PerSeptive Biosystems (Framingham, Massachusetts) was used. Attempts were made to run samples in both positive and negative ion modes. Since the sulfonated polymer chains are intrinsically anionic, the negative ion mode gave superior spectra and was used throughout this investigation. The other polymers were run in the positive ion mode using silver as the cationization agent.

RESULTS AND DISCUSSION

TLC Results

Five samples including proton-terminated PS (spot 1), hydroxyl-terminated PS (spot 2), DPE-terminated PS (spot 3), product resulting from path 1 in scheme 1 (spot 4) and product resulting from path 2 (spot 5) were spotted on the same TLC plate. Figure 1 is the TLC image of these five polymers after development by toluene. Sample 5 separated into two spots while the others did not. We name these six spots 1–4, 5-top and 5-bottom, respectively. The spots of 1, 3, and 5-top have very close R_f values (0.8). The R_f of spot 2 is 0.3. The remainder of the spots remained at the origin.

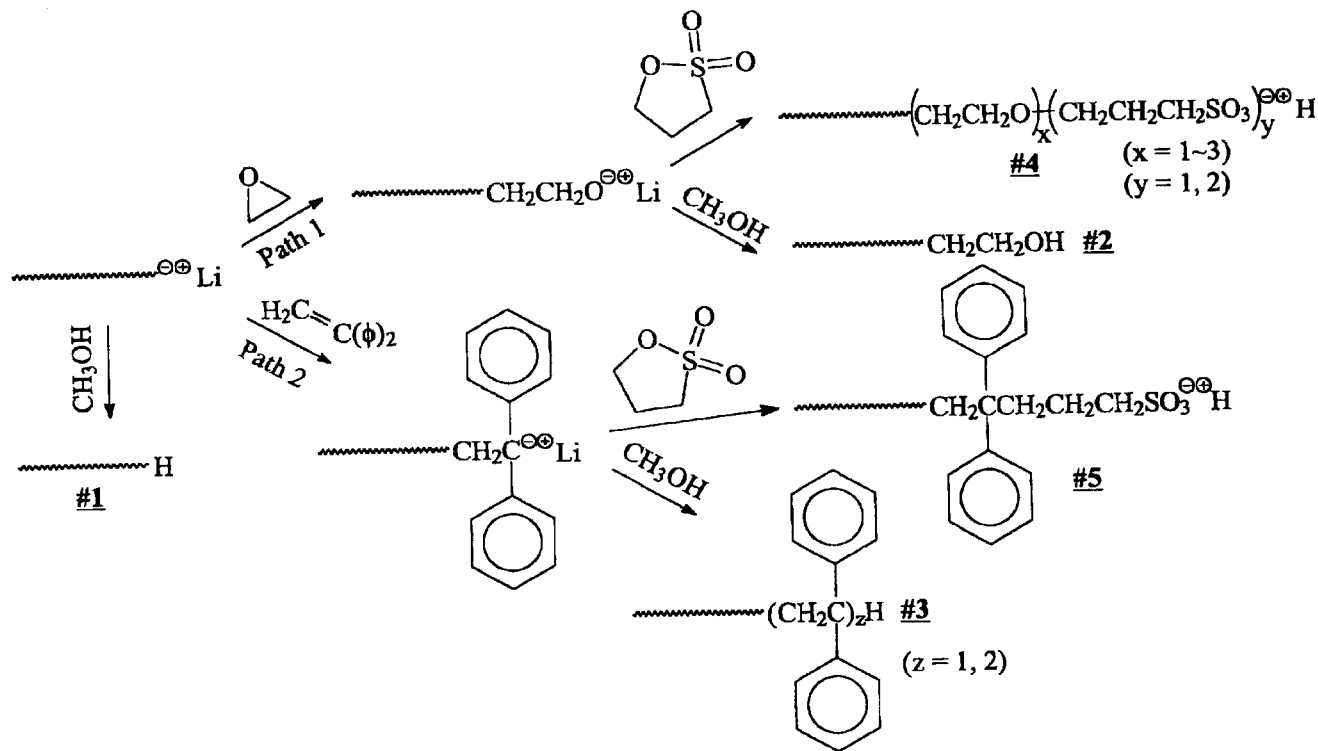
Structural Identification by MALDITOF MS

MALDI-TOF mass spectra were obtained from each of these spots. The MS spectrum of spot 1 (Figure 2) confirms the absence of side reactions in the synthesis of this polymer, showing only peaks separated by the mass of a styrene unit. The spectrum can be seen as representing the expected product PS-H.

The spectra of spots 2 and 3 (Figures 3a and 3b) indicate their structures as PS-CH₂CH₂OH and PS-CH₂C(ϕ)₂H, respectively. The minor peaks present in these two spectra are due to side reactions that were previously considered impossible: propagation of ethylene oxide and DPE in the presence of lithium counterion^[26]. Our other study showed that they are indeed thermodynamically possible but kinetically not favored^[27]. Wesdemiotis et al.^[28] have also recently detected oligomerization of ethylene oxide under similar conditions.

The product from path 1 gives only one spot (spot 4) after TLC development. Its lack of mobility implies that all the polymer chains were end-sulfonated but does not confirm that the synthesis is free from side reactions. Its MALDI spectrum (Figure 4) reveals a series of large peaks representing the expected polymer chain PS-CH₂CH₂O-CH₂CH₂CH₂SO₃⁻, which differs from their neighboring major peak by one styrene unit. Between each pair of neighboring major peaks lie four minor peaks. We believe these peaks are caused by the presence of PS-CH₂-CH₂O-CH₂CH₂CH₂SO₃⁻-CH₂CH₂CH₂SO₃⁻, PS-(CH₂CH₂O)₂-CH₂CH₂-CH₂SO₃⁻, PS-(CH₂CH₂O)₂-CH₂CH₂CH₂SO₃⁻-CH₂CH₂CH₂SO₃⁻ and PS-(CH₂CH₂O)₃-CH₂CH₂CH₂SO₃⁻, respectively, according to their masses. The proposed product structures are shown in Figure 5.

The product from path 2 shows two spots after development (spot 5-top and spot 5-bottom). The MALDI spectrum of spot 5-top is identical to that of spot 3, which is the DPE end-capped PS. The presence of the



SCHEME 1 Synthetic scheme and the structures of the product and by-products.

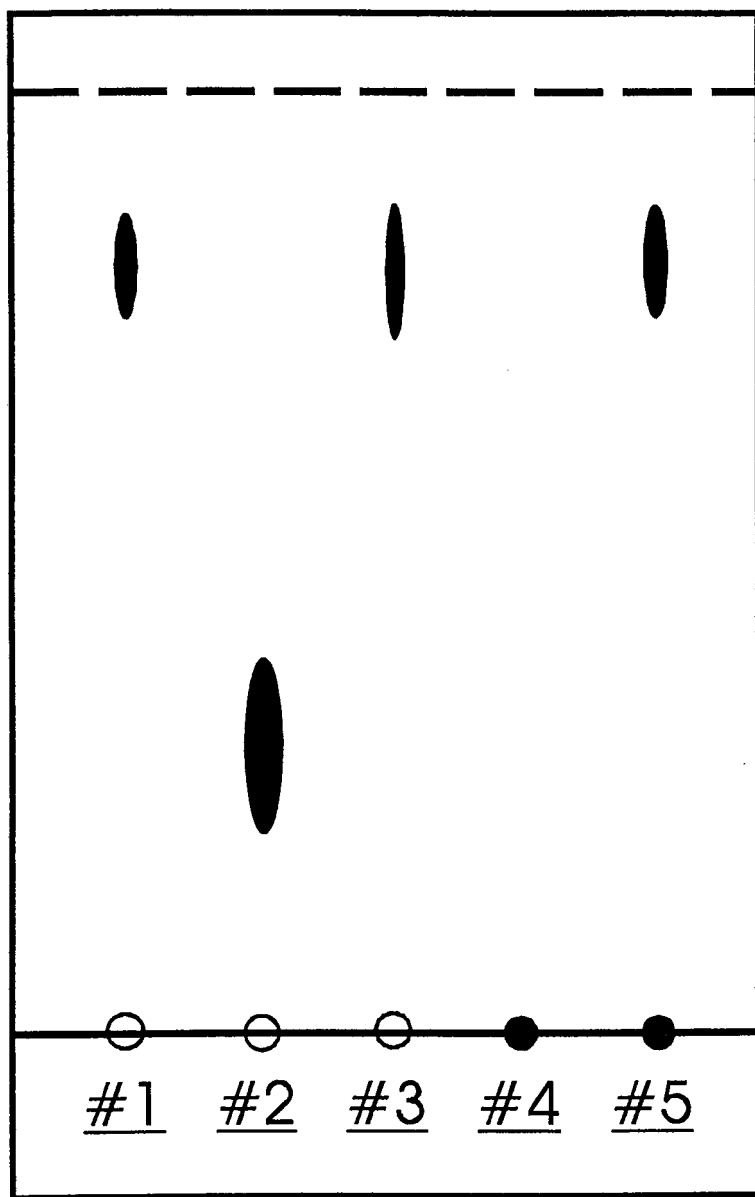


FIGURE 1 TLC image of the five polymer samples.

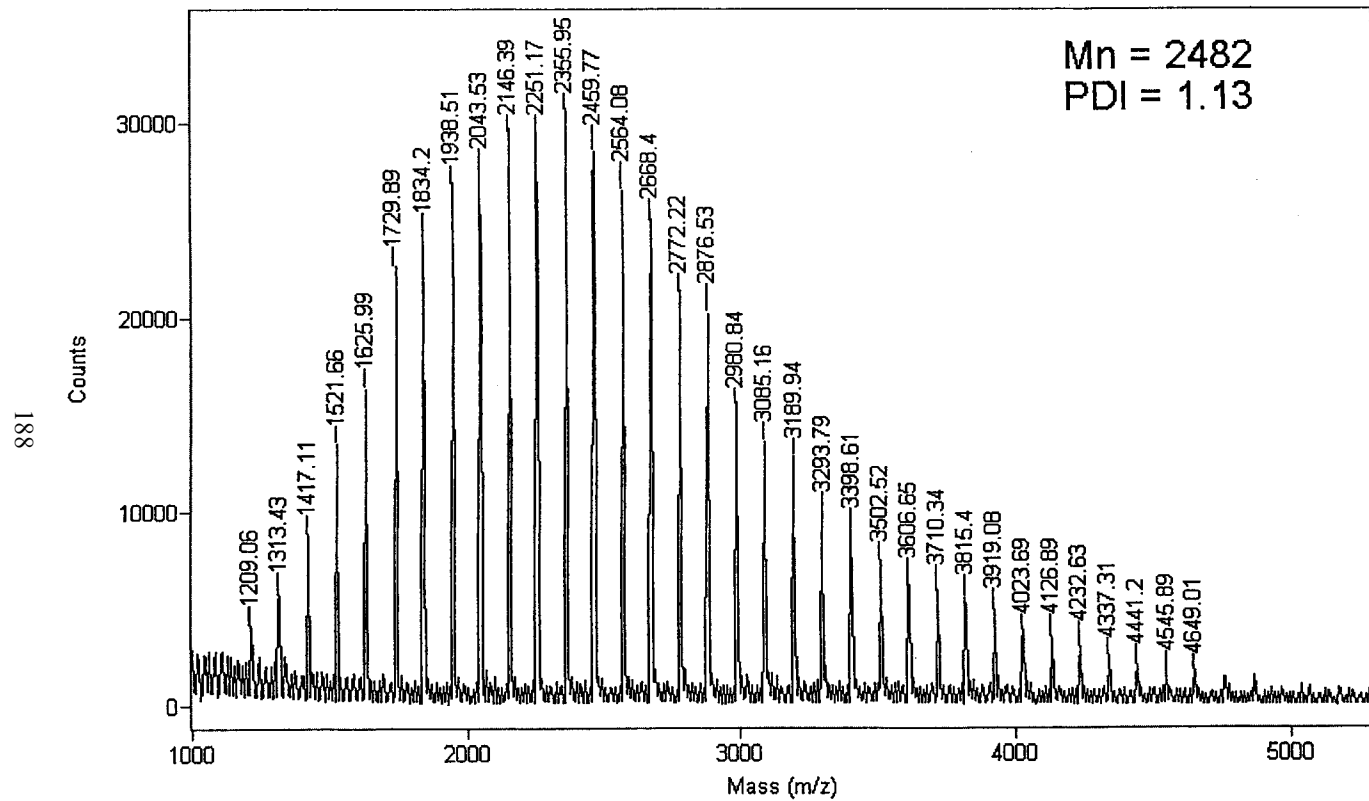


FIGURE 2 MALDI-TOF mass spectrum of spot 1.

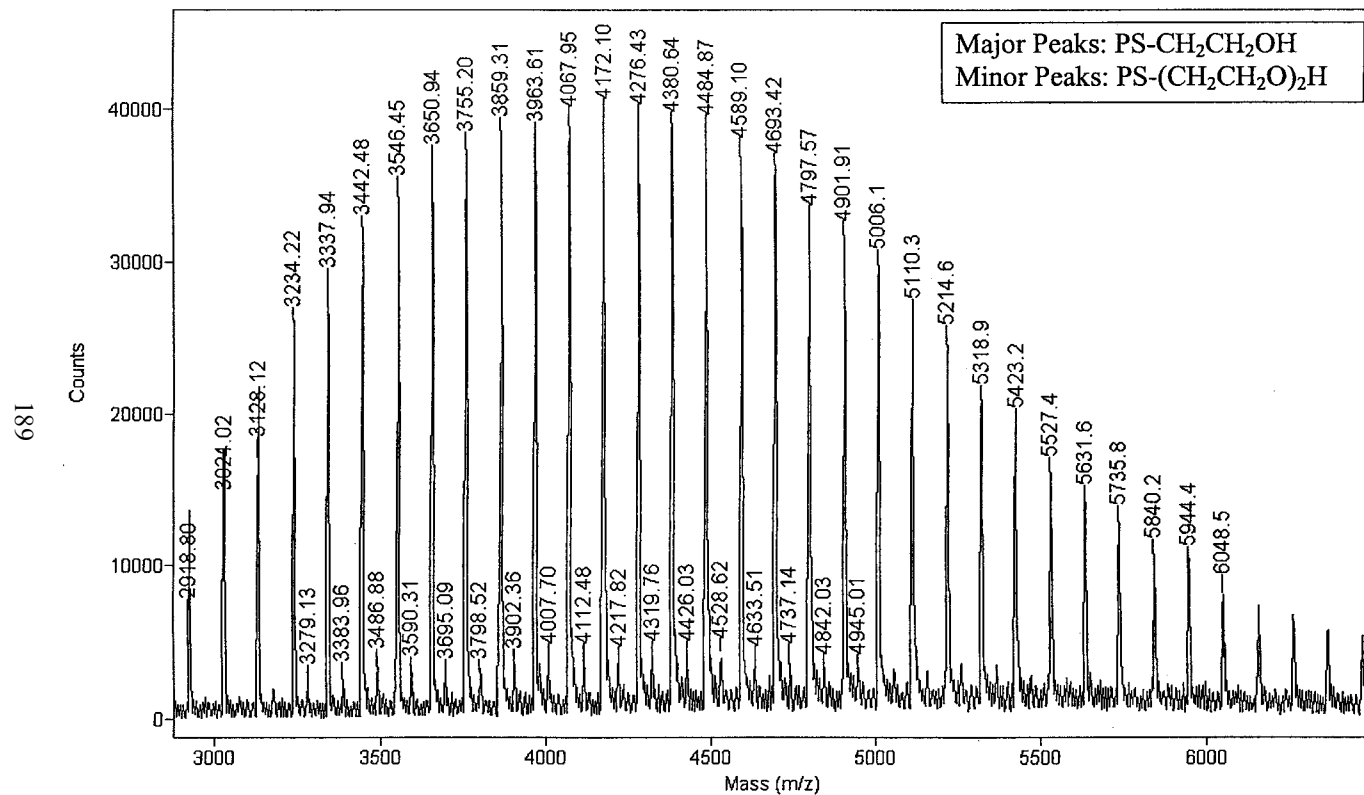


FIGURE 3a MALDI-TOF mass spectrum of spot 2.

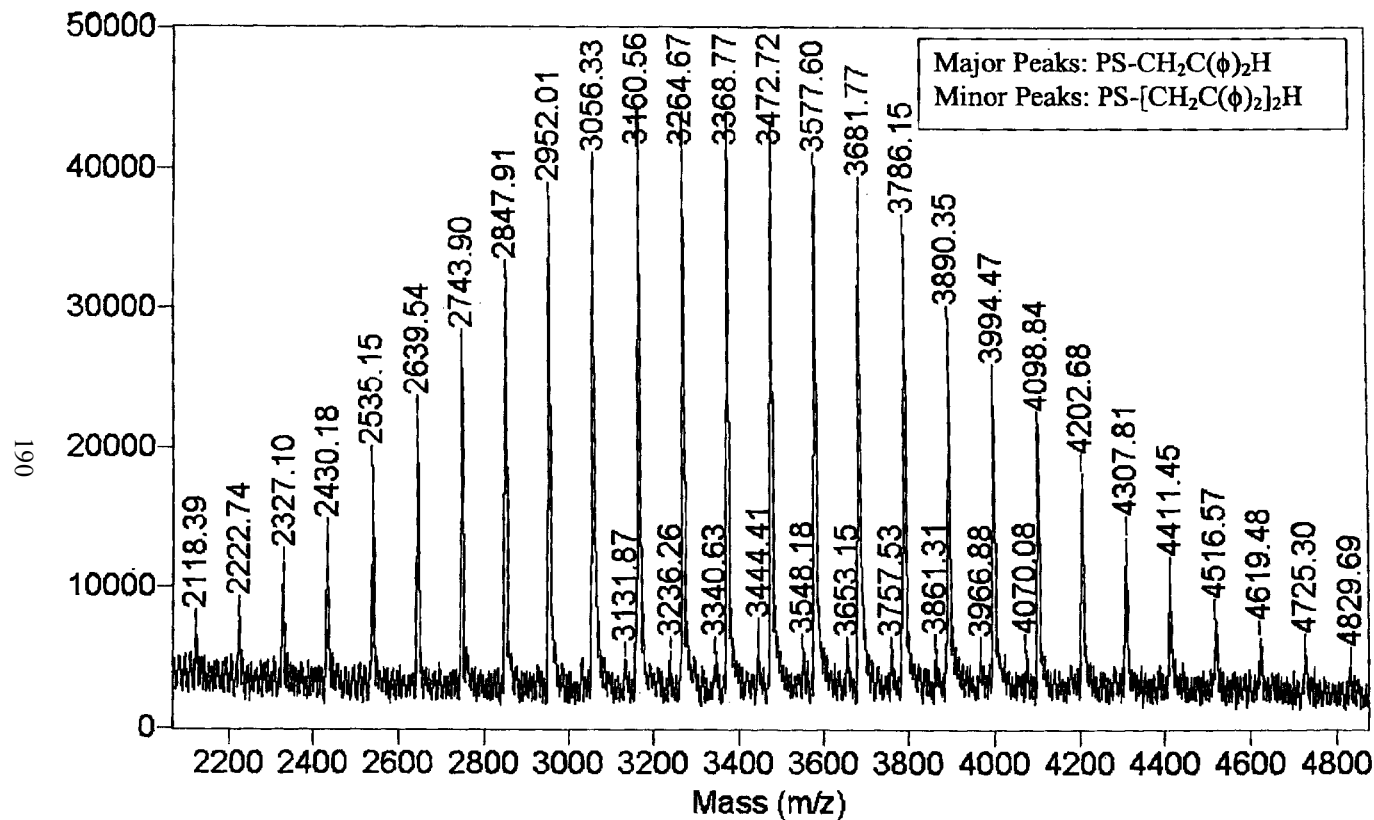


FIGURE 3b MALDI-TOF mass spectrum of spot 5-top.

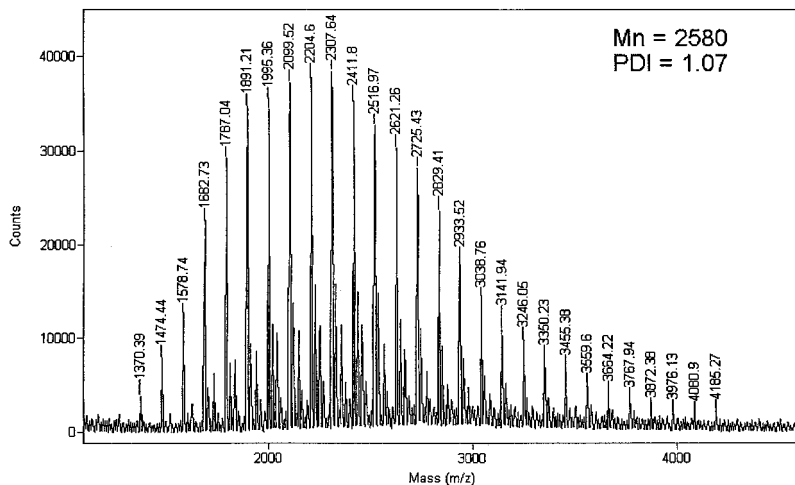


FIGURE 4 MALDI-TOF mass spectrum of spot 4.

by-product $\text{PS-CH}_2\text{C}(\phi)_2\text{H}$ confirms the generation of acidic α -hydrogens from sultone during the reaction, which was suggested by Quirk and Kim^[23]. In the case of path 1, the hydroxyl end groups were still reactive enough to react with the sultone to provide the sulfonated end groups. In the case of path 2, once the living polymers were protonated, the functionalization reaction was halted. The MALDI spectrum of spot 5-bottom is displayed in Figure 6. The major series of peaks were identified as $\text{PS-CH}_2\text{C}(\phi)_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$. In the center of the spectrum, there is a series of small peaks lying between each pair of the neighboring major peaks. They are identified as $\text{PS-CH}_2\text{C}(\phi)_2\text{-CH}_2\text{C}(\phi)_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$, which contains an additional DPE unit.

CONCLUSIONS

We have demonstrated that the power of the combination of TLC and MALDI-TOF MS for the study of polymer synthesis is due to the fact that the separations provided by TLC in composition complement the separation achieved by the MALDI-TOF MS in mass. The result is more clearly and easily interpreted spectra. In the present study, we identified the structures of previously unreported by-products that are produced during the synthesis of end-sulfonated polystyrene. The chemistry is summarized in scheme 1. Path 1 generates end-sulfonated polystyrene while the end group structures differ. Path 2 gives functionalized poly-

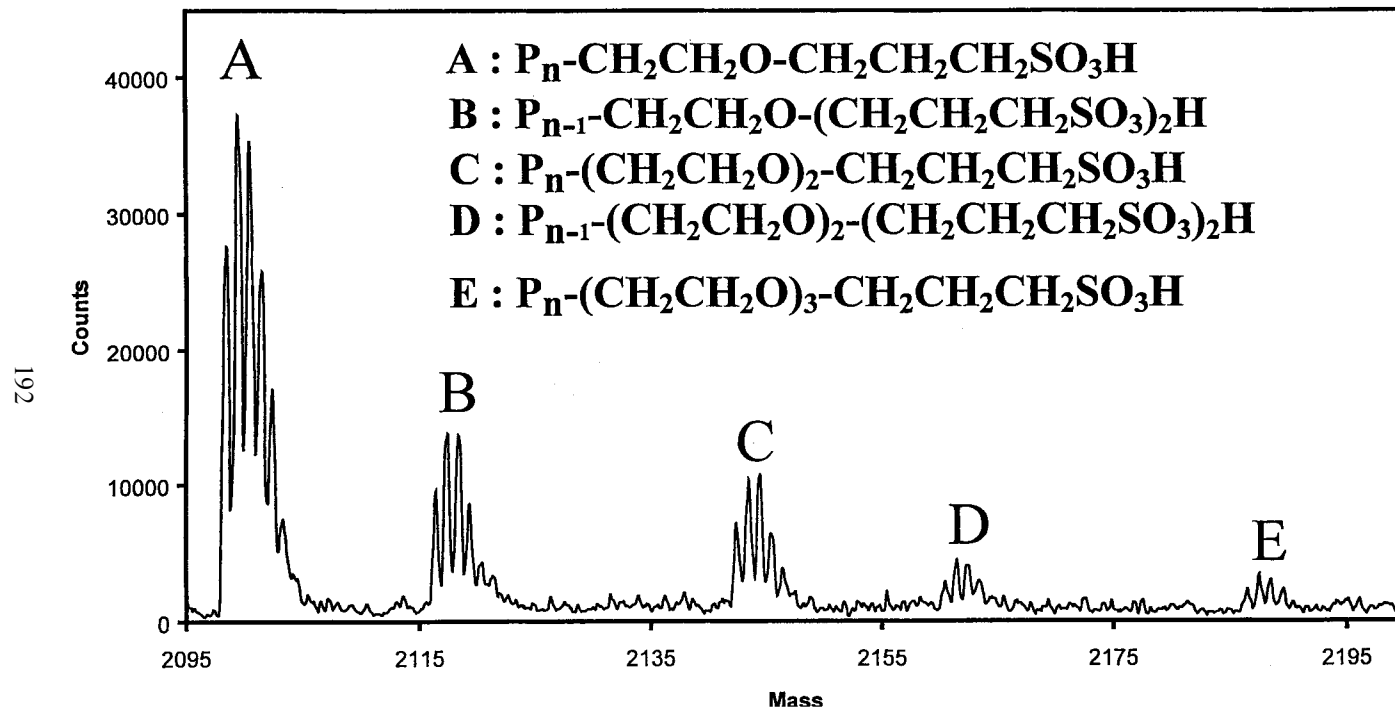


FIGURE 5 Chemical structures of end groups of product from path 1.

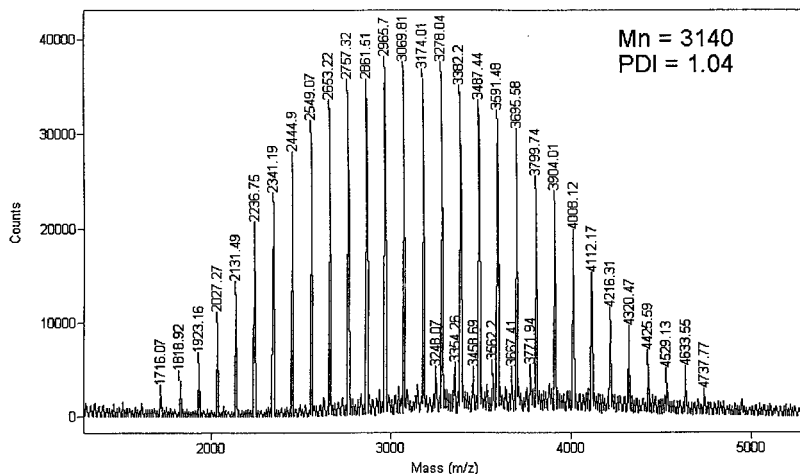


FIGURE 6 MALDI-TOF mass spectrum of spot 5-bottom.

styrene with only one end group structure, but non-functionalized polystyrene is also present to some extent.

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