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Characterization of hydroxyl-end-capped polybutadiene and polystyrene produced by anionic polymerization technique via TLC/MALDI TOF mass spectrometry

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Abstract

A method of off-line coupling of thin layer chromatography with matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (TLC/MALDI-TOF MS) was used to study a synthetic procedure that produces well-defined hydroxyl-end-capped polymers. The TLC separation is based on the structure of the end group of the polymer and is not affected by the degree of polymerization. MALDI-TOF mass spectral analysis of these TLC fractions confirmed their structures. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: TLC/MALDI-TOF MS; Anionic polymerization; Hydroxyl-end-capped

1. Introduction

The recent advent of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) has brought about a promising methodology in the study of chemical structures of polymers, in particular, the determination of their terminal groups [1–4], which are frequently not obtainable or very difficult to obtain from other current analytical techniques. For example, the chemical structure of the terminal functional groups in end-functionalized polymers is difficult to obtain from traditional analytical techniques such as nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, etc., due to the low concentration of these chemical units present in the macromolecules. Impurities must be removed completely, but this is difficult, sometimes impossible, to achieve. MALDI-TOF MS, on the other hand, separates low mass impurities during the TOF process making complete removal of these impurities unnecessary. However, at high molecular weight range, MALDI-TOF MS will fail due to the decreasing mass resolution with the increase of the molecular weights.

The combination of TLC with MALDI-TOF MS is now a routine tool for protein analysis [5,6]. However, it has not been used very often for synthetic polymer characterization despite its simplicity and effectiveness. TLC separates polymers according to the differences in their chemical structure, such as end group or composition of block copolymer, rather than their molecular weights [7–9]. The separation of polymers with different chemical structures prior to MALDI-TOF MS analysis always greatly simplifies the interpretation of the mass spectrum. Thus, this combination shows promise to become an efficient tool for the study of the chemistry of the reactions producing end-functionalized polymers.

In this paper, we report a TLC/MALDI-TOF MS study of the reaction of two kinds of living anionic polymers, having lithium counterions, with ethylene oxide (EO). Polymers produced in this manner, provided the reaction conditions are carefully controlled, should have a well-defined architecture in terms of narrow molecular weight distribution (MWD), predictable molecular weights, and freedom from side reactions [10,11]. Based on the fact that oligomerization was not observed in the products analyzed by NMR or other conventional characterization methods, it has been stated in the literature, with no qualifications on stoichiometry or duration of the reaction, that no propagation of ethylene oxide occurs in anionic polymerization using the lithium counterion. Our present work clearly shows that this is false and that propagation does occur slowly. Since the ionization efficiency is affected by the

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nature of the end groups [12], we cannot make a quantitative determination of the relative amounts of the polymers and impurities caused by propagation of EO here.

2. Experimental

All chemicals used in these syntheses were purchased from Aldrich Chemical Co. (Milwaukee, WI). The initiator, *sec*-butyllithium, was synthesized in-house by the reaction of *sec*-butyl chloride with lithium granules. Anionic polymerization of both styrene and butadiene using *sec*-butyllithium were carried out in benzene at room temperature for 24 h in all-glass reactors using standard all-glass high vacuum techniques [13,14]. The ethylene oxide was purified by allowing it to stand over sodium–potassium alloy for 30 min after drying over calcium hydride. Other reagents in the syntheses were purified as per standard all-glass high vacuum anionic polymerization techniques. The number-average molecular weight (M_n) of the polybutadiene was designed to be 1.5×10^3 Da and this was confirmed by ^{1}H NMR. The polystyrene was designed to have a M_n of 4.0×10^3 Da. That value was confirmed by terminating a small portion of the living poly(styryl)lithium with degassed methanol and subjecting it to gel permeation chromatography (GPC) analysis. The hydroxyl-end-capped polymer was not used in this analysis due to the interaction of the hydroxyl group with the stationary phase of the GPC column.

Chain end hydroxylation was affected by reacting the living anions with ethylene oxide ([ethylene oxide]/[Li] = 4). The functionalization reactions were allowed to work up for different periods as described in Section 3 before they were terminated using degassed methanol. All polymer samples were purified by precipitation in 10-fold excess methanol. Under this very poor solvent condition, polymers immediately formed a white precipitate with no development of turbidity in the methanol. In the case of PBD, an antioxidant was added to methanol to prevent oxidation of the polymer during the precipitation process. Both polystyrene and polybutadiene were dried under vacuum and stored at 0 °C in order to minimize degradation of the polymers.

TLC plates (200μ, 50/p, with fluorescent indicator F-254) purchased from Scientific Absorbents Inc. (Atlanta, GA) were employed to prepare polymer fractions for MALDI-TOF MS analysis. The polymers were dissolved in toluene to make 10% solutions. Plates were intentionally overloaded in order to exaggerate the signal from products present in very small amounts. In the case of hydroxyl-end-capped PBD, 99:1 (v/v) toluene/methanol mixture was used as the developing solvent. In the case of hydroxyl-end-capped PS, the mobile phase was 99.5:0.5 (v/v) toluene/methanol mixture. 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.

The Voyager Elite MALDI-TOF mass spectrometer unit was purchased from PE PerSeptive Biosystems (Framingham, MA). All mass spectra were obtained in positive ion and reflectron modes. A 20 mg/ml solution of *trans*, *trans*-1,4-diphenyl-1,3-butadiene (DPB) and 5 mg/ml solution of AgTFA was prepared in THF. A 10 μl volume of the matrix solution was mixed with 10 μl of the above prepared polymer solution and 1 μl of the AgTFA solution. A volume of 0.5 μl of the above mixture was then spotted on the MALDI sample plate and air-dried before analysis.

3. Results and discussion

Fig. 1 displays a MALDI-TOF MS spectrum of the raw products of hydroxyl-terminated PBD. Two distributions can be clearly observed. One distribution consists of relatively large peaks (for instance, 1129.82, 1183.84, etc.) and the second distribution of relatively small peaks (for instance, 1119.77, 1173.95, etc.). The peaks in each distribution are separated by the mass of a monomer unit 54.05 ± 0.08 ($n = 15$) for the distribution of large peaks and 54.04 ± 0.08 ($n = 15$) for the distribution of small peaks), which suggests that these two series of peaks are different from each other only by their end groups. The larger distribution in each figure contains a terminal hydroxyethyl group ($-CH_2CH_2OH$). This was determined by plotting the peak masses versus their degree of polymerization. The resulting linear relation (15 points) was subjected to regression analysis yielding a regressions slope of 54.046 ± 0.004 and an intercept of 211.09 ± 0.08. When the mass of the cation used for cationization of the sample (^{109}Ag, isotope) was subtracted from the intercept along with the mass of the initiating species (a butyl group, 57.12), the result was 44.97 ± 0.08, which is nominally the mass of a hydroxyethyl group. Here, it is worth mentioning that, in all our MALDI-TOF mass spectra, peaks that were caused by silver ion addition show in a 1:1 doublet pattern that is separated by two mass units, reflecting the isotopic patent of the ‘natural’ silver. Peaks caused by ^{109}Ag were chosen for use in our calculations discussed above. Using the same method, the smaller peak distribution was determined to contain a terminal hydroxyethoxyethyl group ($-CH_2CH_2OCH_2CH_2OH$) with an experimental mass of 88.93 ± 0.06.

Fig. 2(a) shows the MALDI-TOF mass spectra of the raw products of hydroxyl-terminated PS, which was allowed to proceed for 1 day. Only one distribution of peaks representing PS–CH_2CH_2OH can be found in this spectrum. This result corroborates the findings in a previous report about this reaction [15], which claimed that ethylene oxide does not oligomerize in the presence of poly(styryl)lithium in hydrocarbon media. However, a recent publication reported that MALDI-TOF MS analysis found three byproducts in polymers made by essentially the same synthetic procedures [16]. The end group structures of the

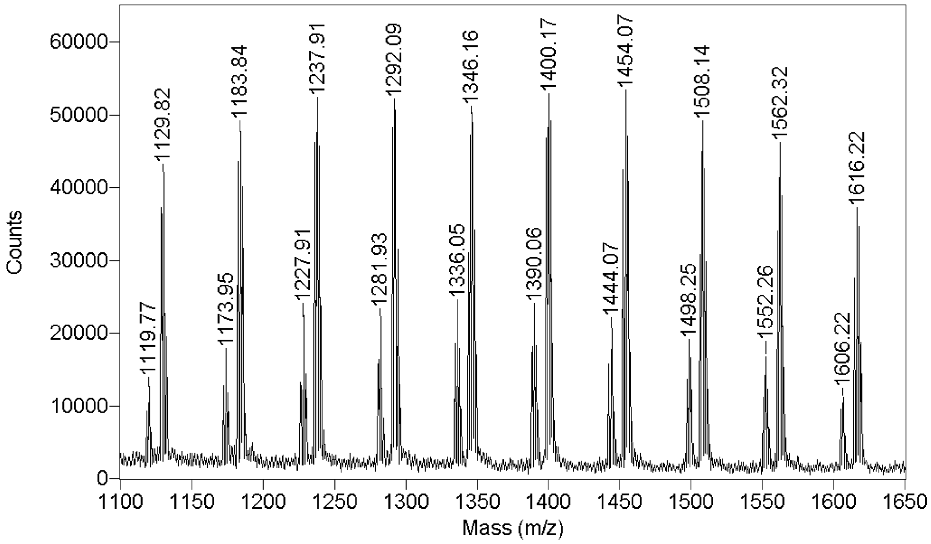

Fig. 1. MALDI-TOF MS spectra of a raw product of hydroxyl-terminated PBD.

byproducts were assigned to be (A) $-CH_2CH_2OCH{=}CH_2$, (B) $-CH_2CH_2O-CH_2CH_2OH$ and (C) $-H$. The presence of (A) was hypothesized to arise from the dehydration of (B).

Since our reaction conditions are essentially the same as the conditions indicated in their publication [16], we then tested whether aging the reaction mixture would give rise to these byproducts. The reaction was allowed to proceed for a month, with a sample for analysis withdrawn after two weeks. MALDI-TOF MS analysis of these samples indicates that the amount of byproduct, relative to the expected product, increases with reaction time. A MALDI-TOF mass spectrum of the reaction mixture, which was aged for 1 month, is shown in Fig. 2(b). Our spectra give no evidence of A and C. Efforts to reproduce the mass spectral work in this paper by using dithranol as the MALDI-TOF MS matrix yielded no such products. We conclude that the end group structures in our sample were different from those reported in the above work [16], presumably caused by a different work-up procedure (i.e. acid or base) for A and presence of impurity during synthesis for C.

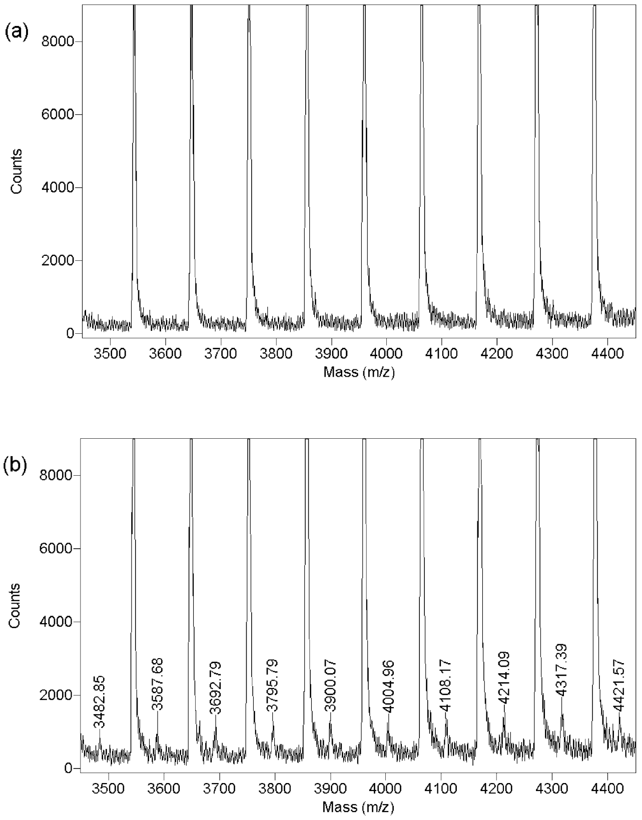

Fig. 2. MALDI-TOF mass spectra of hydroxyl-terminated PS with (a) 1-day and (b) 1-month work-up time.

In order to confirm that the peaks observed in our MALDI spectra are present in the products and are not compounds formed in the mass spectrometer, we attempted to separate the two distributions seen in Fig. 1 by TLC. Fig. 3 displays the TLC image of a proton-terminated PBD (#1) and a hydroxyl-terminated PBD (#2). A mixture of toluene and methanol with volume ratio of 99:1 was used as the developing solvent. The polymer was dissolved in toluene to make a 10% (w/v) solution in order to insure that enough samples remained after the separation to allow high quality mass spectra to be obtained. For this reason oblong spots arose from the hydroxyl-terminated PBD sample after TLC development indicating that the plate was overloaded. When collecting polymer fractions for MALDI-TOF MS analysis, we divided these long spots at the middle and avoided samples near the division point.

Also displayed in Fig. 3 are MALDI-TOF mass spectra of the three spots noted as a, b and c on the TLC image. Fig. 3(b) and (c) displays only one distribution of peaks and gave good agreement with the corresponding distribution in Fig. 1 thus indicating that the impurity peaks were indeed byproducts of the chemical reaction. A similar result was found with the hydroxyl-terminated PS whose reaction time was 1 month.

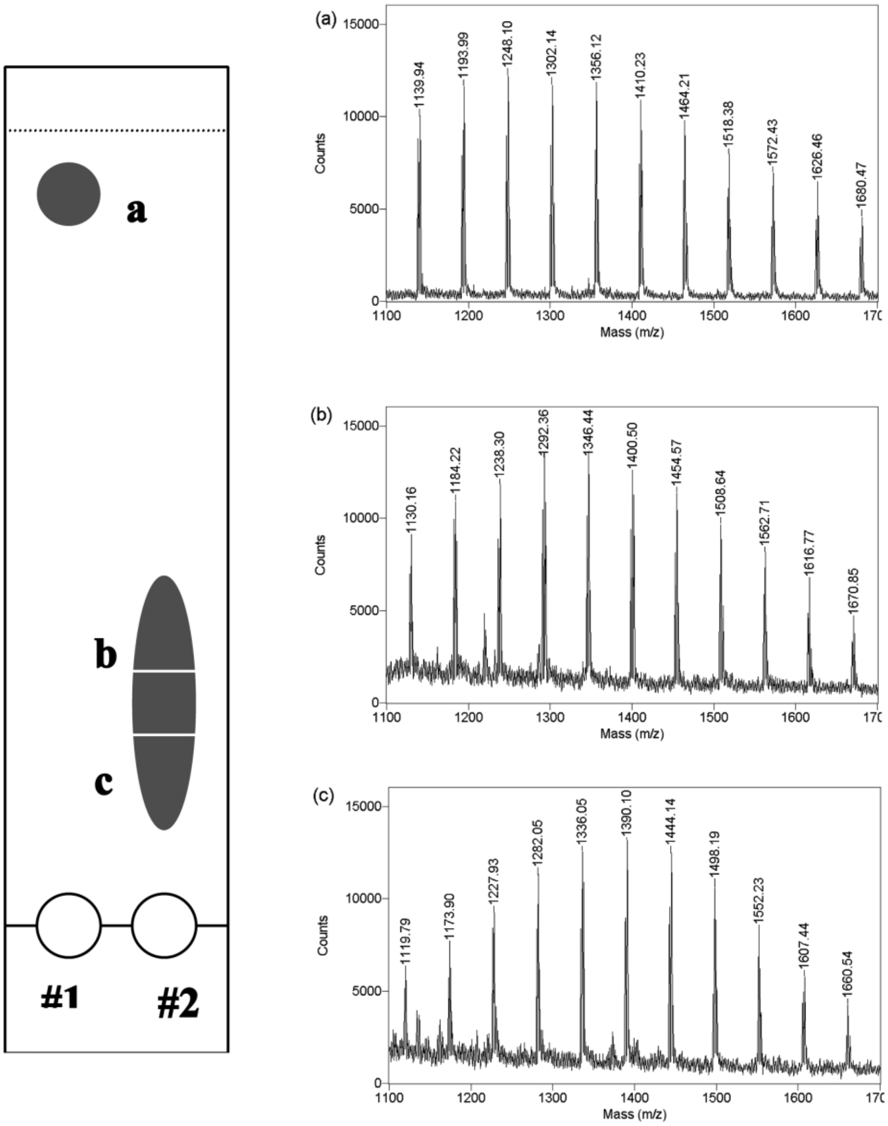

Fig. 3. TLC image of (#1) proton-terminated PBD and (#2) hydroxyl-terminated PBD (mobile phase: toluene and methanol with volume ratio of 99:1) and MALDI-TOF mass spectra obtained from the three spots: a, b, and c.

In summary, the combination of TLC and MALDI-TOF MS is a simple yet efficient tool for probing the end-functionalization reactions of polymers. Therefore, this method can be used to screen chemistry and optimize reaction conditions to produce maximum yields of the desired products. It has been demonstrated here that polymers having a hydrocarbon backbone, such as PS and PBD, and differing only by one unit of ethylene oxide, can be separated by TLC under selected conditions, regardless of differences in the degree of polymerization. Additionally, we found that the degree of ethylene oxide oligomerization depends on the type of living anion, and is much more pronounced with PBD than PS. It should be emphasized that the oligomerization in the case of PS is so slow that PS–CH_2CH_2OH with a uniform end group structure can be obtained under normal functionalization procedures (i.e. 24 h reaction time).

Acknowledgments

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