Characterization of Polyisobutylene by Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

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ABSTRACT: A novel method of matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis of isobutylene homopolymers is reported in this paper. Because of the difficulty in attaching ions for such materials, the ionization for MALDI-TOF MS analysis is realized by sulfonating the olefin end groups to introduce a readily ionized moiety into the polymer. Polyisobutylene samples obtained from both living cationic polymerization and industrial procedures are studied here. The number-average molecular weights and weight-average molecular weights of these materials were also measured by laser light scattering and vapor pressure osmometry. Results obtained from the three techniques agree closely with one another except for the fraction having the highest molecular weight. We postulate that this is due to the range of the molecular weight of this sample being too broad to be accurately measured by MALDI-TOF MS.

Introduction

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) has attained increasing interest as a characterization tool for synthetic polymers in recent years.[1−3] Many efforts have been devoted to the development of optimal experimental conditions for MALDI-TOF MS investigation of a large number of polymer systems, yet certain polymers, for example polyolefin homopolymers, are still not amenable to MALDI analysis. It is generally believed that the lack of suitable ionization sites on the aliphatic backbone of polyolefins makes MALDI analysis of these polymers difficult.

The ionization of synthetic polymers is usually by ion attachment. Polymers with different chemical structures have different affinity toward the type of cations. It is only experimental experience that shows that polar polymers having heteroatoms will show cationization after being mixed with sodium or potassium salts, which coordinate with the heteroatoms, while unsaturated polymers without heteroatoms such as polystyrene, polybutadiene, and polyisoprene can be successfully ionized after the addition of silver or copper salts, which interact with the π-electrons in these polymers. Polymers without any of these ion-binding sites, such as polyolefins, have to be ionized by other methods in order to be subjected to MALDI analysis.

Two methods of promoting the ionization of polyisobutylene (PIB) for MALDI-TOF MS analysis have been documented.[4,5] The first one, reported by Peiffer and co-workers, shows that MALDI spectra of poly(isobutylene-*co*-*p*-methylstyrene) (PIB−PMS) copolymer are obtainable since silver or copper ions may be easily attached to the PMS block.[4] By this method, the ionization of the PIB−PMS copolymer is molecular weight dependent since samples with molecular weights higher than 2000 Da are not readily analyzed. The second method involves incorporation of functional groups that can easily bind ions into the PIB sample.[5] The paper displays a MALDI mass spectrum of a PIB sample having a phenyl group in the middle (initiating species) and two hydroxyl groups (by modifying the two end chlorines resulting from the cationic polymerization into two hydroxyl groups) at the chain ends. The spectrum contains two distributions of peaks. The major distribution was caused by the presence of the dihydroxyl-terminated PIB and the minor one by monohydroxyl-terminated PIB. The presence of the peaks caused by monohydroxyl-terminated PIB in this MALDI mass spectrum indicates that part of the terminal double bonds in the sample failed to be hydroxylated.

A nonquantitative modification is not preferred, especially for PIB samples with only one reactive site, because biased results will be obtained since part of the molecules are not spectroscopically visible. Thus, it is important to find a quantitative chemical modification method in order to make MALDI a useful tool for routine characterization of polyisobutylene. In this respect, a sulfonation scheme reported by Storey and co-workers is suitable. It involves the reaction of olefin-terminated polyisobutylenes with acetyl sulfate at room temperature. Quantitative sulfonate end-capped polyisobutylenes are obtainable according to the document.[6,7] The reactions are shown in Figure 1. PIBs having *tert*-chlorine end groups can also be converted into sulfonate end-capped PIBs by the same procedure.

This method is superior to that of Peiffer et al. or Zsuge et al. because sulfonated polymers are intrinsically anions. Polymers having a sulfonate group give good MALDI-TOF mass spectra without the use of any

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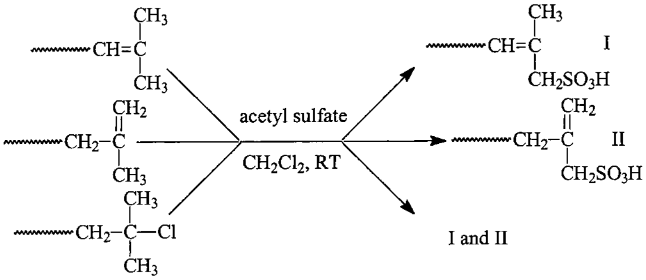

Figure 1. Reaction scheme of end sulfonation of polyisobutylene samples.

ionization reagent.[8] In the cases of the two published methods, the implanted ionization sites have to physically attach an ion before the polymers were ionized. This limits these methods to only low molecular weight PIB samples because at higher molecular weights the polymer chains are long enough to hinder the physical meeting of the ionizing sites and the ions.

In the current work, we examine the feasibility of applying this sulfonation reaction to routine MALDI-TOF MS analysis of polyisobutylene homopolymers. Experiments were carried out on both well-defined PIB produced by living cationic polymerization and four narrowly distributed fractions of an industrially produced PIB samples. The MALDI-TOF MS results were compared to those obtained from conventional techniques including vapor pressure osmometry (VPO) and light scattering (LS) in order to determine the advantages and limitations of the proposed method.

Experimental Section

Materials. Living cationic polymerization of IB was carried out according to a published procedure[9] using the following conditions: [IB] = 2.0 M, [TMPCl] = 0.054 M, [DtBP] = 0.002 M, [$TiCl_4$] = 0.08 M, methylcyclohexane/methyl chloride (60/40, v/v) cosolvent, −80 °C. Low molecular weight PIB fractions were obtained from a commercial sample by fractionation using the solvent/nonsolvent method. Matrix materials used in MALDI-TOF MS analysis were purchased from Aldrich Chemical Co. and used without further purification. All MALDI-TOF mass spectra reported in this paper were generated using the *all-trans*-retinoic acid matrix. Tetrehydrofuran (THF) was used as solvent for both polymers and the matrices.

Sulfonation. The sulfonation of all PIB samples employed in this study was done according to a published procedure[7] with minor modification. In a dry beaker were combined 20 mL of CH_2Cl_2 and 7 mL of acetic anhydride. Concentrated sulfuric acid (2.3 mL) was added to this mixture with stirring over a period of 10 min. This acetyl sulfate solution was then added to a 0.01 M solution of PIB in CH_2Cl_2. This resulting reaction mixture was kept in a 50 °C water bath, with stirring, for 3 h. Then the reaction mixture was slowly poured into 500 mL of 0.1 M aqueous NaOH solutions with stirring. The pH value of the water phase was monitored. If the solution went acidic, more NaOH solution was added until it became slightly basic. The polymer floated on the surface of the water. The wet polymers were collected, and excess water was removed by pressing them between two pieces of filter paper, following by vacuum-drying for at least 1 day.

MALDI-TOF MS Measurements. All MALDI spectra were obtained using a Voyager Elite mass spectrometer (PE PerSeptive Biosystems, Framingham, MA). A 10 mg/mL matrix solution and a 10 mg/mL polymer solution were prepared in THF. A volume of 10 μL matrix solution was then mixed with 2 μL of the polymer solution. An aliquot of 0.5 μL of the resulting mixture was spotted on the MALDI sample plate and air-dried before analysis. All spectra were obtained in the negative ion mode.

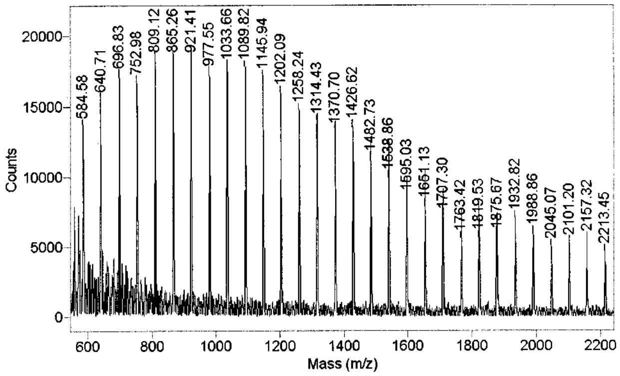

Figure 2. MALDI-TOF mass spectrum of a polyisobutylene sample synthesized by cationic polymerization using TMPCl as initiator.

SEC-MALLLS Measurements. Light scattering measurements were done at room temperature using a DAWN DSP-6 instrument (Wyatt Technology Inc.) equipped with a He−Ne laser (λ = 633 nm) and a multiangle laser light scattering (MALLS) detector. The photometer was calibrated with pure toluene and was connected to a SEC system equipped with three columns (two Waters HT6E linear columns and a Waters HT3 column whose average pore size is 10^3 Å) and a refractive index (RI) detector (Waters 2410) from which the concentration of each position of the peak was determined. THF was used as the eluent whose flow rate was set to 1 mL/min. Polymer sample solutions were prepared in three different concentrations (1×10^{-3}, 2×10^{-3}, and 3×10^{-3} g/cm^{-3}) and injected using a sample loop of 0.1 cm^{-3} capacity.

The specific refractive index increments of THF solutions (d*n*/d*c*) were taken to be 0.1027, 0.1098, 0.1107, and 0.1123 cm^3/g for the four PIB fractions from low to high molecular weight, respectively.[10] The angular dependence of the scattering intensity was analyzed using Berry's square-root plot to determine the mean-square radii of gyration $\langle S^2 \rangle$ at each position of the peak.

VPO Measurements. At each increment of solute concentration, the osmolalities of three aliquots of each of the four PIB fractions were measured in succession using a UIC 070 VPO unit (Joliet, IL). Toluene (40 °C) was the solvent in all cases. Benzil (210 g/mol) was used to calibrate the instrument.

Results and Discussion

Current ionization methods in MALDI-TOF MS are not suitable for isobutylene homopolymers even though these polymers typically have a double bond at one or both termini. These terminal double bonds, however, can serve as reaction sites in chemical modification for introducing functional groups that can ionize the polymer more efficiently. Here we propose a method of obtaining MALDI-TOF mass spectra from isobutylene homopolymers which involves conversion of the terminal double bonds into sulfonate groups in quantitative yield.

We first tested the method on a monofunctional PIB sample (PIB-Cl) produced by living cationic polymerization using TMPCl as initiator. Figure 2 shows a portion of the MALDI-TOF mass spectrum of this sample after the sulfonation procedure. From the regression analysis of a plot of the masses of these peaks vs their degree of polymerization, a linear relationship with a regression slope of 56.137 ± 0.002 and intercept of 135.49 ± 0.04 was obtained. This indicates the polymer consists of a number of C_4H_8 units and two end groups that have a total mass of 135.49 Da. According to the cationic polymerization chemistry, the sample should have a proton at the α-terminus. Thus, the end group at the ω-terminus would consist of a sulfonate

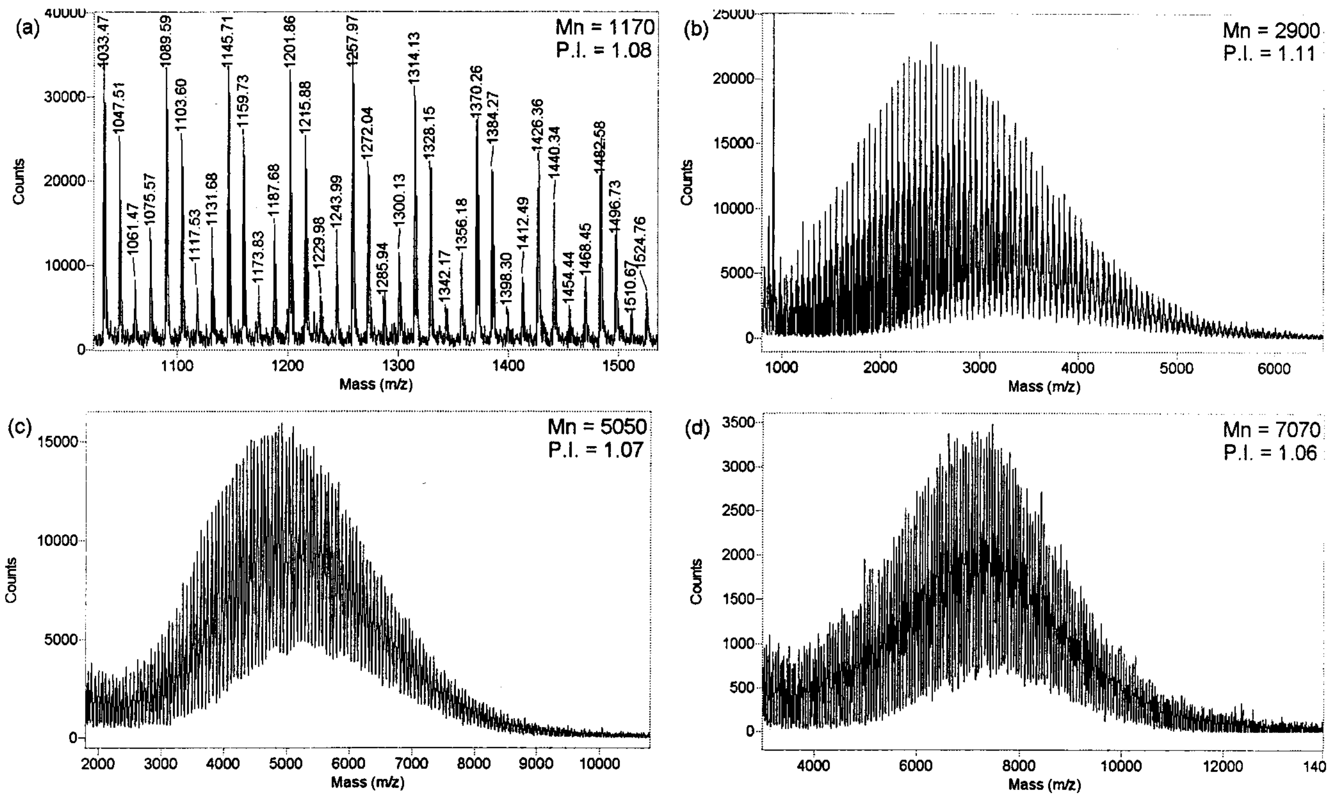

Figure 3. MALDI-TOF mass spectra of four fractions obtained from an industrially produced PIB sample

group (MW = 80.05 Da) and an unsaturated isobutylene repeat unit (C_4H_6, 54.09 Da), as predicted from the known sulfonation chemistry.

We next tested the method on commercial PIB samples. To the best of our knowledge, we are the first to report MALDI-TOF MS investigations on industrially produced PIB samples. It was necessary to fractionate the commercial polymer samples prior to analysis because MALDI-TOF MS tends to underestimate the molecular weights and molecular weight distributions of board distribution samples. To obtain sufficient amounts of fractionated samples for chemical modification, the solvent/nonsolvent method was chosen. Four fractions were obtained and were named as PIB-1 to PIB-4.

Table 1 lists MALDI-TOF MS, SEC-MALLS, and VPO data for these four PIB fractions. All three techniques agree well with each other for fractions PIB-1, PIB-2, and PIB-3. In testing the fraction with the highest molecular weight, we found that different matrix materials give different values for number-average molecular weight ranging from 3.5 × 10^3 to 7.1 × 10^3 Da. All these values are significantly smaller than those from SEC-MALLS. We believe that the anomalously low average molecular weights found for PIB-4 by MALDI-TOF MS were caused by the fact that the range of molecular weights in this higher molecular weight sample was substantially wider than the range of molecular weights in the lower molecular weight samples PIB-1, PIB-2, and PIB-3. It is well-known that MALDI-TOF MS is limited in its ability to obtain spectra over large molecular weight ranges and will in these cases tend to yield spectra that emphasize the lower molecular weight species and discriminate against higher molecular weight species. The data reported in this paper were obtained from the use of *all-trans*-retinoic acid, which gave the highest average molecular weight values among all matrices tested. VPO data are not obtained for PIB-4 because this sample exceeds the high mass limit of the workable range of the VPO technique.

Table 1. Analysis Data of Four PIB Fractions Obtained from MALDI-TOF MS, VPO, and SEC-MALLS

	MALDI-TOF MS		SEC-MALLS		VPO
	M_n	PI	M_n	PI	M_n
PIB-1	1.17 × 10^3	1.08	1.23 × 10^3	1.10	1.1 × 10^3
PIB-2	2.90 × 10^3	1.11	2.88 × 10^3	1.10	3.0 × 10^3
PIB-3	5.05 × 10^3	1.07	5.98 × 10^3	1.10	5.8 × 10^3
PIB-4	7.07 × 10^3	1.06	10.6 × 10^3	1.10	not done

Figure 3a–d shows the MALDI-TOF mass spectra of these four fractions. In Figure 3a–c, four distributions are clearly seen. Within a given distribution, peaks are separated by a mass of 56.14 ± 0.06 Da. This means that each distribution represents a PIB with different end groups. The end groups differ from each other by an integral number of methylene units ($-CH_2-$, 14.02 Da). This is expected because, unlike the PIB from living polymerization, the commercial sample is produced at high temperature in a process that is chain transfer dominated and characterized by carbenium ion rearrangements, β-scission reactions, and other high-energy processes. This leads to molecules with a variety of end-group structures, including those with irregular carbon numbers, i.e., those in which the total number of carbon atoms is not evenly divisible by four. Although some minor structures remain unresolved, most of the major end groups in commercial PIB have now been clearly identified.[11–13]

Conclusions

A novel method for MALDI-TOF MS analysis of isobutylene homopolymers is reported herein. It involves sulfonation of olefin end groups to introduce a readily ionized moiety into the PIB. Good agreement can be found between MALDI-TOF MS and conventional characterization techniques including VPO and LS except for fraction PIB-4, which has the highest average molecular weights. We believe that MALDI-TOF MS underestimated the average molecular weight of PIB-4 due to the broad range of molecular weights containing this fraction.

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