Characterization of Polyisobutylene Succinic Anhydride Chemistries Using Mass Spectrometry

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ABSTRACT: Representative Polyisobutylene succinic anhydride (PIBSA) samples have been studied by different MS techniques including Electrospray Ionization Fourier Transform Ion Cyclotron Resonance MS (ESI-FTMS) (positive and negative modes), Atmospheric Pressure Chemical Ionization Fourier Transform Ion Cyclotron Resonance MS (negative mode), and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (positive and negative modes). Negative ion ESI-FTMS produces the best results. Differences between "mono-succan" and "di-succan" content can readily be observed. The source of the PIBSA (PIBSA-I and PIBSA-II processes) can be easily distinguished and the formation of methyl esters and amide derivatives can provide complementary data. The experiments have demonstrated the capabilities of mass spectrometry to detect and characterize such polymers samples. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2682–2690, 2012

Key words: PIBSA; ESI-FTMS; GPC; additives; mass spectrometry

INTRODUCTION

Most mechanical equipment utilized in today's world requires the use of a lubricant to work effectively. Usually, a lubricant consists of the composition of base oil (i.e., mineral oils) and additives.[1] One of the main functions of the base oil is the reduction of friction between two moving surfaces. Also, it provides protection against wear particles, prevents corrosion and oxidation, and transfers heat (reducing heat as a result of the friction), among others.[2] However, to increase the capacity and efficiency of the lubricant (i.e., petroleum-based, synthetic), it needs the addition of additives. Lubricating additives are classified in different categories based on their characteristics. Some of the characteristics are: to improve the existing physical properties of the base oil, to protect the lubricant (by limiting the chemical change or deterioration), and the machine (from failure of the lubricant).[1–4] Among the major categories of additives that have been established are: antioxidants, antiwear agents, corrosion inhibitors, friction modifiers, dispersants, detergents, and others. It is for that reason that one of the main goals of lubricant research is trying to find better additive technologies.

Polyisobutylene succinic anhydride (PIBSA)[4–8] and PIBSA-derived products are key lubricant additive technologies. PIBSA-based dispersants are found in almost all engine oil formulations and many other lubricant types. Additionally, PIBSA itself is used as an additive in a variety of products. PIBSA and PIBSA-based products are also used in nonlubricant business areas such as emulsion explosives.[9] Actual product performance of these materials depends greatly on the specific attributes of both the starting hydrocarbon polymer (C4-olefin derived) and the resulting PIBSA produced by reactions of the olefinic polymer with maleic anhydride (MAA).[7,8] Variables include differences in both the structure and size (M_w) of the hydrocarbon tail, how it is attached to the succinic anhydride (SA) groups, and the degree of succination.

Because of the obvious importance of these chemistries, characterization of PIBSAs is crucial. Over the years, a number of analytical techniques and methods have been used to provide key information enabling the continued development and production of these materials. Everything from wet chemical methods (i.e., TAN = Total Acid Number), chromatography techniques (i.e., GPC), and spectroscopic methods (i.e., FTIR, NMR) have been and continue to be used. NMR in particular has been utilized to provide detailed characterization of structural

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TABLE I
PIBSA Sample Matrix[a]

PIBSA	M_n (PIB)	PIBSA-type process	PIB : MAA	GPC results	
				M_n	M_w
Sample 1	1000	I	1 : 1.25	1212	1860
Sample 2	2300	I	1 : 1.5	2930	5142
Sample 3	1000	II	1 : 1.3	1152	2266
Sample 4	1000	II	1 : 1	1196	2183
Sample 5	1000	II	1 : 2	1128	2248
Sample 6	2000	II	1 : 1.95	1936	4607
Sample 7	2000	II	1 : 1.5	2112	5062

[a] PISSA, polyisobutylene succinic anhydride; PIB, poly isobutylene; M_n, number average molecular weight; M_w, weight average molecular weight; I, PIBSA-process I (highly reactive PIB); II, PIBSA-process II (less reactive PIB); MAA, maleic anhydride.

differences between various PIBSA types.[10] Mass spectrometry (MS) techniques have found some use in the characterization of PIBSA and some PIBSA-derived chemistries, but has not generally been used as a core technique.[11–13] MS offers the potential of rapidly providing both structural and molecular weight distribution information.

In this work, a comparison study of different MS techniques, including Electrospray Ionization Fourier Transform Ion Cyclotron Resonance MS (ESI-FTMS),[14–28] Atmospheric Pressure Chemical Ionization Fourier Transform Ion Cyclotron Resonance MS (APCI-FTMS),[14,16,29] and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF)[14,21,30–37] to characterize various PIBSA samples is presented. The goal of this study is to determine the best MS technique(s) for rapid, accurate characterization of PIBSAs and see if additional information, not currently available from other techniques, can be determined.

EXPERIMENTAL

Materials

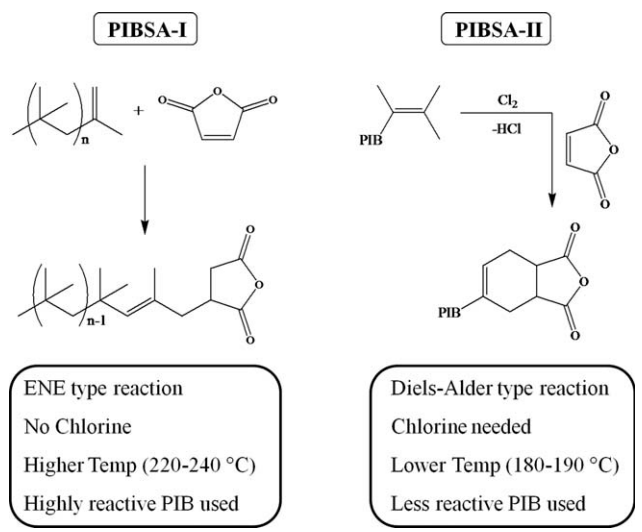
The solvents acetonitrile (CH_3CN), methanol (CH_3OH), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), and sodium hydroxide [NaOH, 50% (w/w) solution] were purchased in HPLC grade from J. T. Baker (Phillipsburg, NJ). Sodium Iodide (NaI, 99.5%) and ammonium hydroxide (NH_4OH, 28.0–30.0%) were purchased from Alfa Aesar (Ward Hill, MA) and EMD Chemicals (Gibbstown, NJ), respectively. All the chemicals or reagents were used as received. The PIBSA samples were provided by The Lubrizol (Wickliffe, OH).

GPC

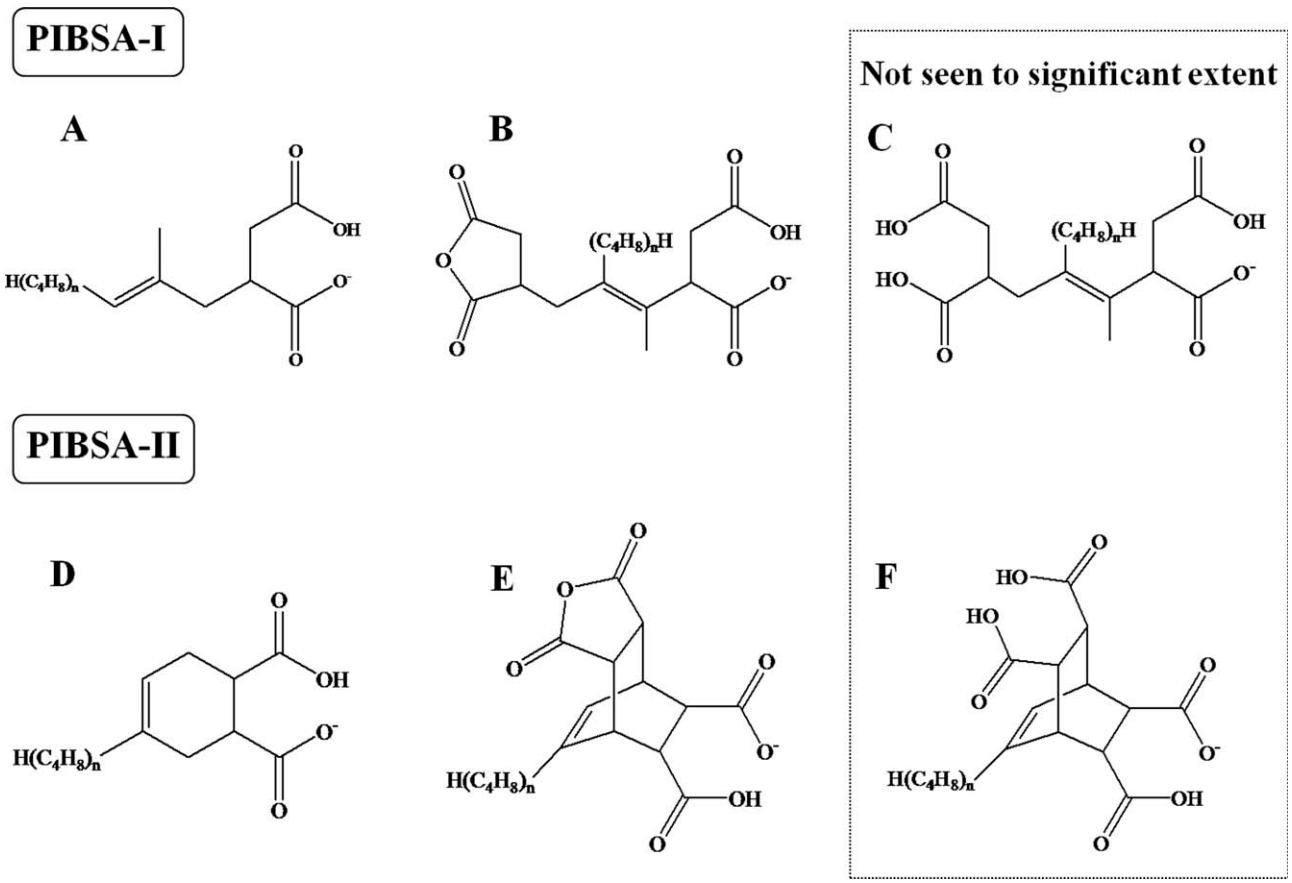
To have an approximation of the molecular weight (M_w and M_n) of the samples, they were analyzed by Gel Permeation Chromatography (GPC). GPC analysis was performed using a Waters 2690 Separations Module Alliance instrument equipped with a refractive index (RI) detector. The instrument calibration was performed using 14 narrow poly(isobutylene) standards ranging from 226–1,020,000 Da (Polymer Standards Service, Warwick, RI). Samples were filtered with a 0.2 mmpolytetrafluoroethylene filter prior to injection. The column set consisted of three Mix-C and one 100 Å columns, 300 × 4.6 mm^2 i.d., (PL gel type from Polymer Labs) were used. Others conditions for the experiments include the mobile phase (THF), the flow rate (1.0 mL/min), the column temperature (40°C), injection volume (300 μL), RI sensitivity (16), RI scale factor (20), and sample concentration (5 mg/mL). Data workup was performed using Waters Empower software (version 1.0).

FTICR

Mass spectral data were obtained using a Bruker Apex 47e Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with an Analytica of Branford API 100 electrospray source. The electrosprayed solutions for negative ion ESI-FTMS were prepared by dissolving 1 mg of PIBSA in 1 mL of THF (1 mg/mL). Then, a dilution was made with the addition of a 4 m*M* NaOH in H_2O solution and acetonitrile, reaching the final concentration of 0.1 mg/mL. The solutions were introduced into the mass spectrometer at 2 μL/min via a syringe pump. Nitrogen was used as the nebulizing gas (20 psi) and drying gas (250°C, 10.00 L/min). The capillary voltage was set up to +4411 V and the capillary exits at −119.8 V. Thirty-two scans were averaged per spectrum and the experiments were performed in triplicate.



Scheme 1 PIBSA chemistry.



Scheme 2 Major PIBSA ions seen by negative ion ESI-FTMS.

To obtain complementary information about the PIBSA chemistry, additional preparations using CH_3OH and NH_4OH were used on the samples. For the CH_3OH treatment, the electrosprayed solutions for negative ion ESI-FTMS were prepared by dissolving 1 mg of PIBSA in 1 mL of CH_2Cl_2 (1 mg/mL). Then, a dilution was made with the addition of a 1 m*M* NaOH in CH_3OH solution, reaching the final concentration of 0.1 mg/mL. For the NH_4OH treatment, the electrosprayed solutions for negative ion ESI-FTMS were prepared by dissolving 1 mg of PIBSA in 1 mL of THF (1 mg/mL). Then, a dilution was made with the addition of a 10 m*M* NH_4OH in H_2O and acetonitrile solution, reaching the final concentration of 0.1 mg/mL.

RESULTS AND DISCUSSION

PIBSA chemistry

A series of seven PIBSA samples were selected for this study. A summary that includes the preparation and type of chemical processes utilized for those samples is shown in Table I. The starting polyisobutylene (PIB) samples were not available for GPC analysis. Table I does show the typical production M_n values of the starting PIB samples. The PIBSA samples were analyzed by GPC and the results obtained (M_n and M_w data) agree fairly well with the values expected from the M_n of the starting PIB (see Table I).

Two types of chemical processes were used to synthesize the PIBSA samples and are described here as PIBSA-process I (PIBSA-I) and PIBSA-process II (PIBSA-II). PIBSA-I uses an ENE reaction (Alder-ene reaction)[38,39] between MAA and PIB. The PIBs used have unsaturated groups, which are primarily vinylidene and are very reactive with MAA. The PIB used for PIBSA-I is prepared cationically in the presence of boron trifluoride (BF_3) as the catalyst (Lewis acid catalyst).[4,5,7,11,12] The reaction produces a SA with one of its H atoms substituted with PIB. This process requires high temperatures (usually between 220 and 240°C) and no chlorine is added (see Scheme 1).

On the other hand, PIBSA-II uses a Diels–Alder type reaction[38,39] between MAA and PIB. The PIB used in this process is prepared cationically in the presence of aluminum chloride ($AlCl_3$) as the catalyst. Although, the PIB used in this reaction also have unsaturated groups, a lower proportion of these are vinylidene, making the material less reactive towards MAA.[4,5,7,11,12] This process uses lower temperatures (usually between 180 and 190°C) and

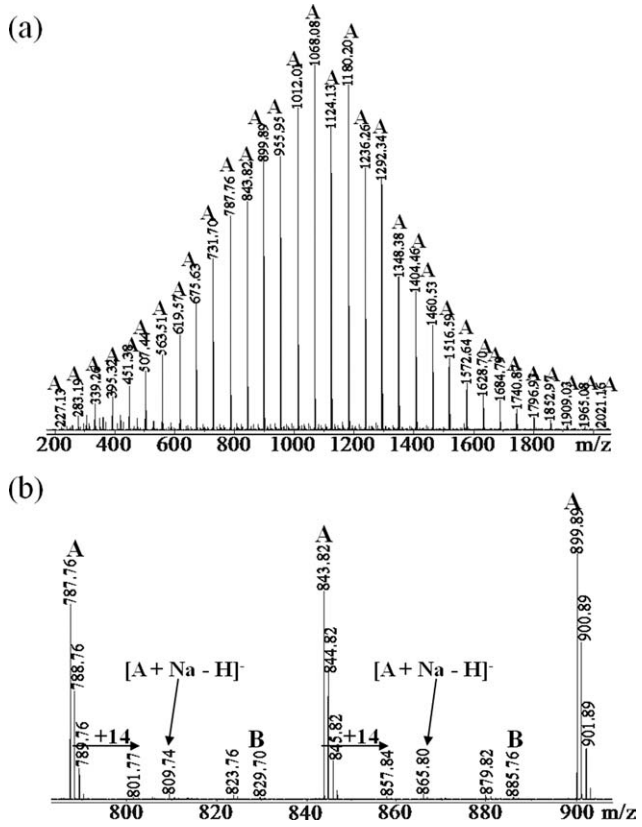


Figure 1 (a) ESI-FTMS mass spectrum of PIBSA (Sample 1). (b) Expanded ESI-FTMS mass spectrum of PIBSA (Sample 1).

chlorine is needed in the reaction to help produce the PIBSA products (see Scheme 1). Some advantages of PIBSA-I versus PIBSA-II process is that the former is chlorine-free (the additives do not contain chlorine) and the resulting additives can give an acceptable engine performance. Both processes continue being utilized by industry because PIBSA from PIBSA-II is generally less expensive than from PIBSA-I.

ESI-FTMS of PIBSA samples using THF/H_2O treatment

PIBSA samples were analyzed by ESI-FTMS in the negative mode under THF/H_2O treatment to form the dicarboxylic acid. Example structures (one possible isomer shown) of the major PIBSA ions seen by negative ion ESI-FTMS are shown in Scheme 2.

PIBSA Sample 1 was prepared through PIBSA-I containing a PIB : MAA ratio of 1 : 1.25 (see Table I). The negative ESI-FTMS mass spectrum and a mass spectrum expansion (range $\sim$ *m/z* 780–910) are shown in Figure 1(a,b), respectively. ESI of Sample 1 produces a series of oligomer ions 56 mass units apart from each other, corresponding to the PIB repeat unit (C_4H_8). The main series ions in the mass spectrum are mostly mono-succinic anhydride ("mono-succan") corresponding to the deprotonated structure "A" (see Scheme 2) and the expected products show a molecular weight distribution around 1000. Some additions of +14 masses (CH_2) to the right of the main series "A" are observed as well as the series with structure "B" at very low intensity. Another small distribution is observed with Na^+ exchanged for a proton ($[A + Na - H]^-$).

PIBSA Sample 2, which was made with a higher MW PIB, was prepared also through PIBSA-I but with a PIB : MAA ratio of 1 : 1.5. ESI of Sample 2 also produces a series of oligomer ions 56 mass units [PIB repeat unit (C_4H_8)] apart from each other (mass spectrum is not shown). Similar to Sample #1, it shows that the main series ions in the mass spectrum are mostly mono-succan, corresponding to the deprotonated structure "A" (see Scheme 2). However, the molecular weight distribution is not as high as expected (Sample #2 has a $M_n = 2300$). The peaks seen 14 *m/z* higher and lower are from differences of CH_2 in the starting PIB. The distribution of $[A + Na - H]^-$ is also observed.

PIBSA Sample 3 was prepared through PIBSA-II with a PIB : MAA ratio of 1 : 1.3 (see Table I). The negative ESI-FTMS mass spectrum and a mass spectrum expansion (range $\sim$ *m/z* 780–910) are shown in Figure 2(a,b), respectively. ESI of Sample 3 produces

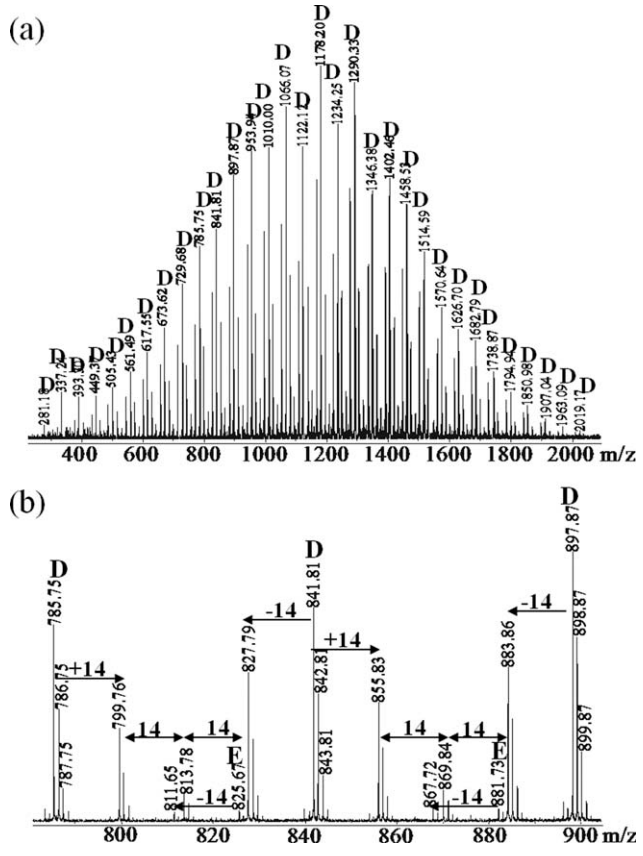


Figure 2 (a) ESI-FTMS mass spectrum of PIBSA (Sample 3). (b) Expanded ESI-FTMS mass spectrum of PIBSA (Sample 3).

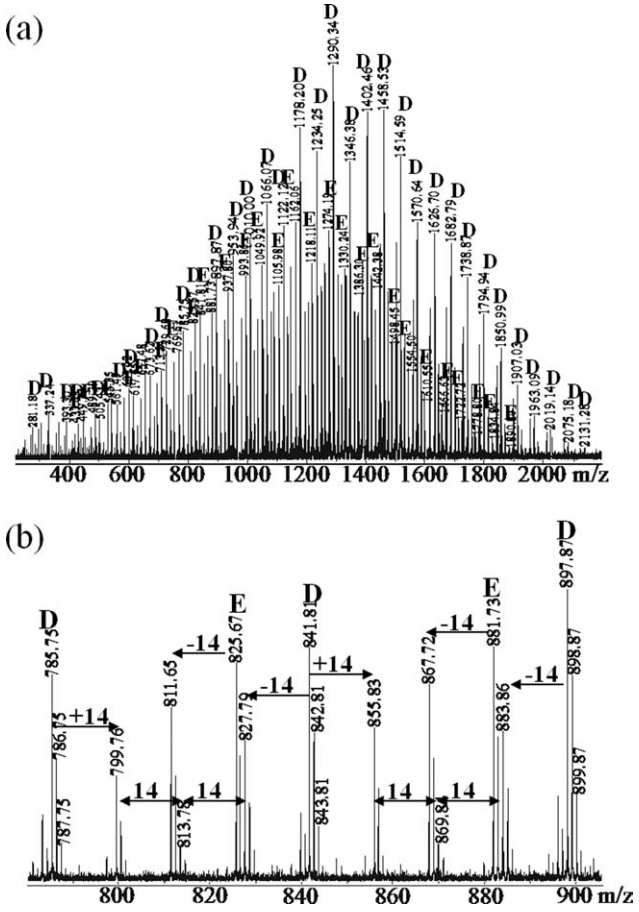


Figure 3 (a) ESI-FTMS mass spectrum of PIBSA (Sample 5). (b) Expanded ESI-FTMS mass spectrum of PIBSA (Sample 5).

also a series of oligomer ions 56 mass units [PIB repeat unit (C_4H_8)] apart from each other. The main series ions in the mass spectrum are identified as mono-succan PIBSA with structure "D" (see Scheme 2). They are shown as the expected products with a molecular weight distribution around 1000 and which includes C3/C5 discontinuities (±14), which is typical of low reactive PIB. Another series is observed with structure "E" which corresponds to di-succinic anhydride ("di-succan") PIBSA. The low intensity of "E" series agrees with the low PIB : MAA ratio used (see Table I).

PIBSA Sample 4 was also prepared through PIBSA-II at PIB : MAA ratio of 1 : 1 in an attempt to produce exclusively mono-succan (no di-succan). The ESI-FTMS spectrum for Sample 4 is similar to that one for Sample 3 with mostly mono-succan (D) and very little di-succan (E) (mass spectrum is not shown).

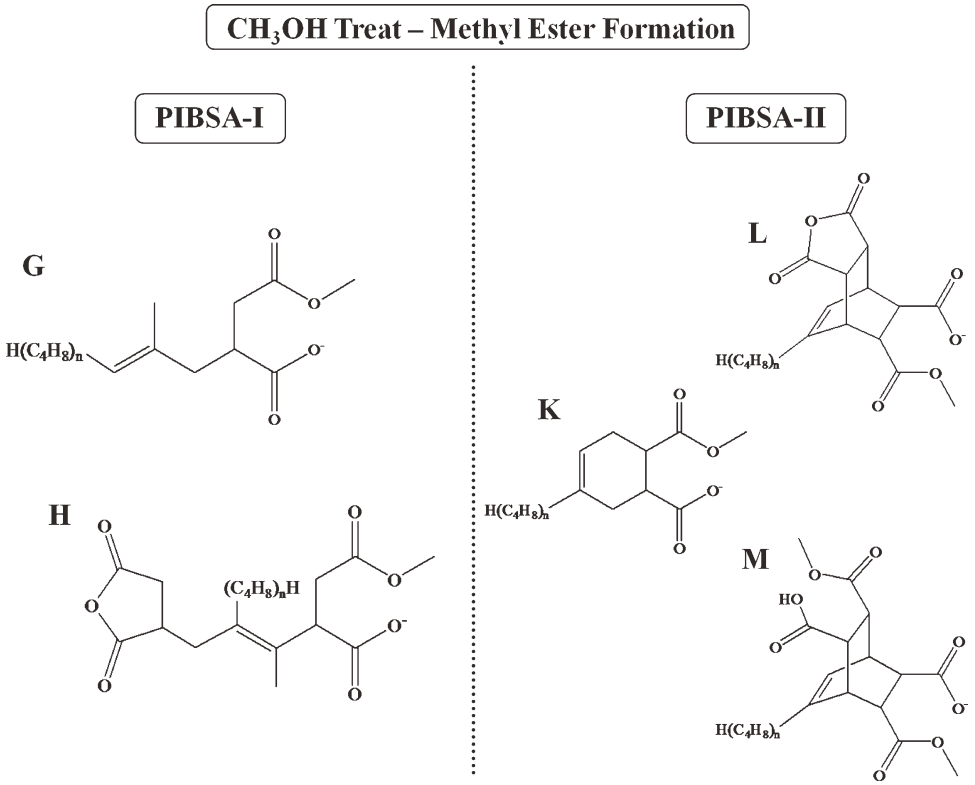
PIBSA Sample 5 was prepared through PIBSA-II at a PIB : MAA ratio of 1 : 2 to try to produce mainly di-succan products (see Table I). The negative ESI-FTMS mass spectrum and a mass spectrum expansion (range ~ *m/z* 780–910) are shown in Figure 3(a,b), respectively. ESI of Sample 5 produces two main series of oligomer ions with 56 mass units [PIB repeat unit (C_4H_8)]. One of these series in the mass spectrum was identified as mono-succan PIBSA with structure "D" (see Scheme 2). The other series, labeled as structure "E" corresponds to di-succan PIBSA. Thus, both di-succan and mono-succan series are clearly observed. The mass spectrum also shows C3/C5 discontinuities (±14) and a molecular weight distribution seen close to 1000. This series "E" (di-succan) is observed at higher intensity, compared to the previous samples discussed, being in agreement with the PIB : MAA ratio used (see Table I).

PIBSA Samples 6 and 7 were prepared through PIBSA-II with PIB : MAA ratios of 1 : 1.95 and 1 : 1.5, respectively, (see Table I). The ESI-FTMS spectra for Samples 6 and 7, are similar to the mass spectra for Samples 3 and 4 (mass spectra are not shown). As expected the amount of di-succan (E) is higher in Sample 6. However, the molecular weight distribution for Samples 6 and 7 were not as high as expected ($M_n = 2000$) (see Table I).

ESI-FTMS of PIBSA samples by CH_3OH and NH_4OH treatments

In this section, PIBSA samples were analyzed by ESI-FTMS in the negative mode under a CH_3OH treatment to promote the methyl ester formation. The major PIBSA ions seen through the CH_3OH treatment by negative ion ESI-FTMS are shown in Scheme 3.

The mass spectrum of PIBSA Sample 1 was examined. The negative ESI-FTMS mass spectrum and a mass spectrum expansion (range ~ *m/z* 790–920) are shown in Figure 4(a,b), respectively. ESI of Sample 1 produces a series of oligomer ions 56 mass units [PIB repeat unit (C_4H_8)] apart from each other. The main series ions in the mass spectrum are mostly mono-succan which correspond to the deprotonated structure "G" (see Scheme 3). The mass spectrum also shows +14 masses (CH_2) lower from the main series "G" and the expected products are seen around 1000 molecular weight distribution. Isobaric peaks were also observed in the mass spectrum [see Fig. 4(b)]. For example, the ion at *m/z* 843.71 corresponds to structure "H," the mono-methylated di-succan, and the ion at *m/z* 843.82 corresponds to structure "A," the diacid of the mono-succan, as seen in Figure 1. PIBSA Sample 2 was also examined (mass spectrum is not shown). The ESI mass spectrum obtained for Sample 2 is similar to Sample 1. However, the molecular weight distribution is not as high as expected (Sample 2 has a $M_n = 2300$). The peaks of 14 *m/z* (CH_2) higher and lower are also observed.



Scheme 3 Major PIBSA ions seen using CH_3OH treatment by Negative Ion ESI-FTMS.

PIBSA Sample 3 was also analyzed using the CH_3OH treatment method. The negative ESI-FTMS mass spectrum and a mass spectrum expansion (range ~ *m/z* 790–920) are shown in Figure 5(a,b), respectively. ESI of Sample 3 produces a series of oligomer ions 56 mass units [PIB repeat unit (C_4H_8)] apart from each other. The main series ions in the mass spectrum are identified as mono-succan PIBSA with structure "K" (see Scheme 3). They are seen as the expected products with a molecular weight distribution around to 1000. The C3/C5 discontinuities (±14) are also observed. PIBSA Sample 4 was also analyzed and the ESI mass spectrum obtained is similar to Sample 3 (mass spectrum is not shown).

The CH_3OH treatment method was also used for PIBSA Sample 5. The negative ESI-FTMS mass spectrum and a mass spectrum expansion (range ~ *m/z* 780–910) are shown in Figure 6(a,b), respectively. ESI of Sample #5 produces three main series of oligomer ions 56 mass units [PIB repeat unit (C_4H_8)] apart from each other. The first of the series ions in the mass spectrum are mostly mono-succan which correspond to the deprotonated structure "K" (see Scheme 3). The second and third series correspond to the structures "M" and "L" di-succan PIBSAs, respectively. Thus, both di-succan and mono-succan series are clearly observed in the mass spectrum. Series "K" is seen at the higher intensity series followed by "M" and "L." However, the latter two

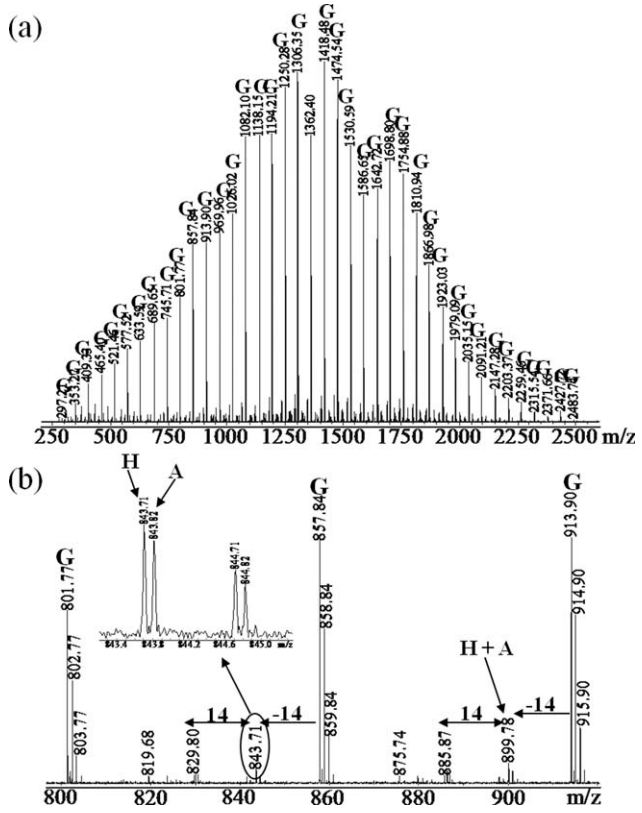


Figure 4 (a) ESI-FTMS mass spectrum of PIBSA (Sample 1). (b) Expanded ESI-FTMS mass spectrum of PIBSA (Sample 1). Note: CH_3OH treatment was used.

series ("M" and "L") are observed in a high intensity level, being in agreement with the PIB : MAA ratio established (see Table I). The C3/C5 discontinuities (±14) are also observed and the molecular weight distribution is seen close to 1000. PIBSA Samples 6 and 7 were also analyzed and the ESI mass spectra obtained are similar to Samples 3 and 4 (mass spectra are not shown). However, the molecular weight distribution for Samples 6 and 7 were not as high as expected ($M_n = 2000$).

PIBSA Sample 1 also was analyzed by ESI-FTMS in the negative mode using NH_4OH treatment to form the amide carboxylic acid. The major PIBSA ions seen by negative ion ESI-FTMS using NH_4OH treatment are shown in Scheme 4.

The negative ESI-FTMS mass spectrum and a mass spectrum expansion (range ~ *m/z* 770–910) are shown in Figure 7(a,b), respectively. ESI of Sample 1 produces a series of oligomer ions 56 mass units [PIB repeat unit (C_4H_8)] apart from each other. The main series ions in the mass spectrum are mostly mono-succan corresponding to the deprotonated structure "I" (see Scheme 4). Another series was detected that correspond to the di-succan with "J" structure. The expected products are seen around 1000 molecular weight distribution. Some additions of +14 masses (CH_2) are observed to the right of the main "I" series.

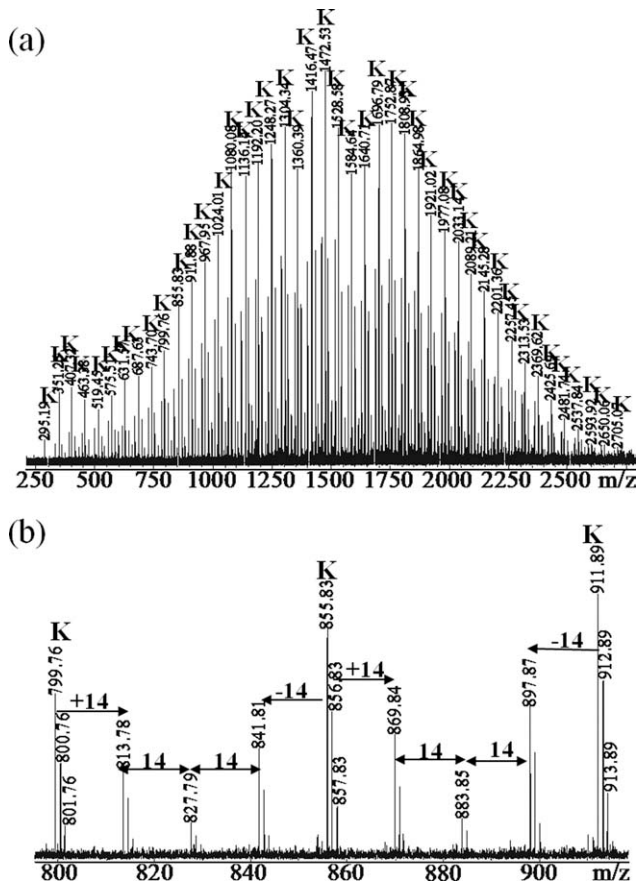


Figure 5 (a) ESI-FTMS mass spectrum of PIBSA (Sample 3). (b) Expanded ESI-FTMS mass spectrum of PIBSA (Sample 3). Note: CH_3OH treatment was used.

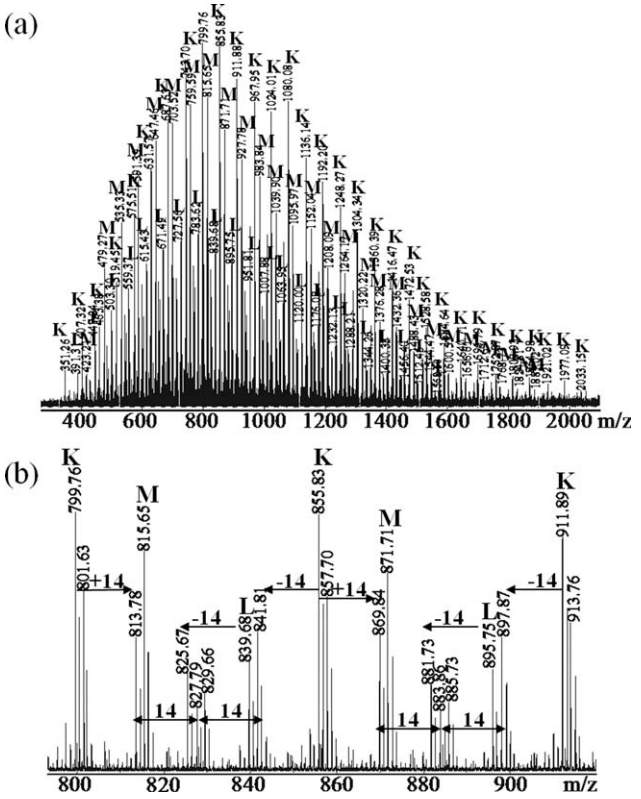
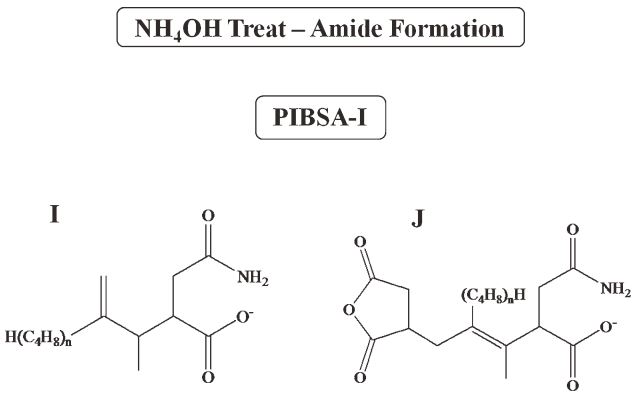


Figure 6 (a) ESI-FTMS mass spectrum of PIBSA (Sample 5). (b) Expanded ESI-FTMS mass spectrum of PIBSA (Sample 5). Note: CH_3OH treatment was used.

Analysis of PIBSA by other treatments and techniques

PIBSA samples were also analyzed using different preparations by ESI-FTMS instrumentation. For example, the samples were dissolved in THF (with the addition or elimination of acetonitrile) and different concentrations of the NaOH in H_2O solution



Scheme 4 Major PIBSA ions seen using NH_4OH treatment by negative ion ESI-FTMS.

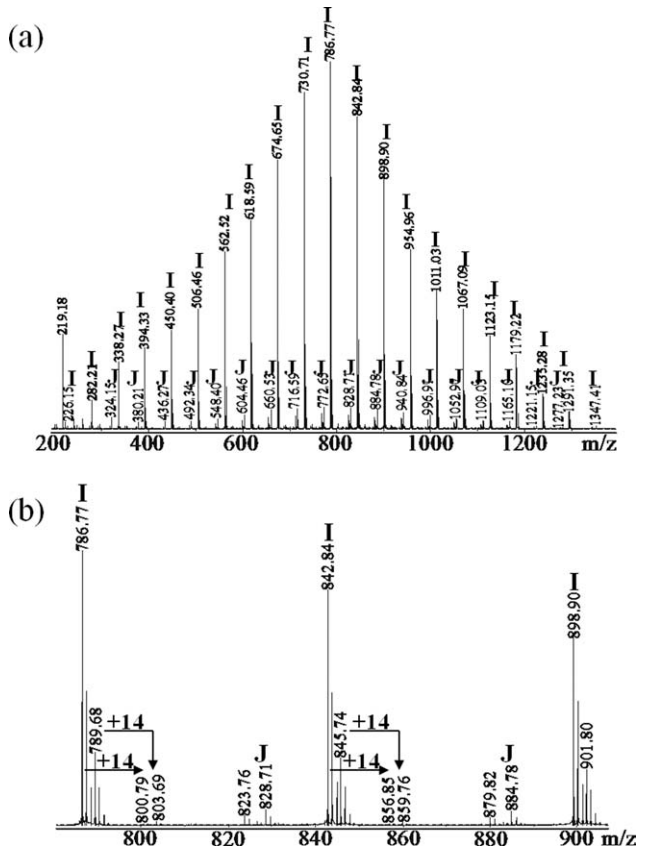


Figure 7 (a) ESI-FTMS mass spectrum of PIBSA (Sample 1). (b) Expanded ESI-FTMS mass spectrum of PIBSA (Sample 1). Note: NH_4OH treatment was used.

such as 20, 10, and 0.4 m*M* were tried. All different combinations of solvents and concentrations produced very low molecular weight distributions or even no detection. Positive ESI-FTMS was also tried with no success.

Both positive and negative MALDI-ToF was also employed for PIBSA analysis with minimal success. Different sample preparations were used. For example, PIBSA samples were dissolved in different solvents (e.g., THF and CH_2Cl_2). Also, several matrices (e.g., dithranol and sinapinic acid) and salts additions were tried (e.g., NaI, NaTFA, LiTFA, AgTFA, and NaOH).

Negative APCI-FTMS was used as another MS technique for PIBSA analysis. Negative ion APCI-FTMS was not very repeatable as finding consistent tuning parameters was difficult. This may have been due to decarboxylation (loss of CO_2) during the APCI process.

CONCLUSIONS

Representative PIBSA samples have been studied by different MS techniques including ESI-FTMS (positive and negative modes), APCI-FTMS (negative mode), and MALDI-ToF (positive and negative modes). Negative ion ESI-FTMS (THF : ACN w/4 m*M* NaOH in H_2O) produces the best results. Mass spectra generated molecular weight distributions are relative and do not typically give overall accurate measure of full distribution. Differences between mono-succan and di-succan content can readily be observed but additional work is needed to explore accuracy for quantitation. The source of the PIBSA (PIBSA-I and PIBSA-II processes) can be easily distinguished. The formation of methyl esters and amide derivatives can provide complementary data. Positive ion ESI-FTMS does not work well and low molecular weight distributions were produced. Also, negative ion APCI-FTMS spectra were not very repeatable and the tuning process in the instrument was difficult to achieve. MALDI-ToF technique was not straightforward, but can be explored further.

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