Negative Ion Electrospray Ionization Mass Spectrum of Polyisobutenylsuccinic Anhydride: Implications for Isobutylene Polymerization Mechanism

James J. Harrison,* Cecilia M. Mijares, Michael T. Cheng, and James Hudson

Chevron Oronite Company LLC, 100 Chevron Way, Richmond, California 94802-0627, and Chevron Research and Technology Co., 100 Chevron Way, Richmond, California 94802-0627

Received October 16, 2001

ABSTRACT: Polyisobutenylsuccinic anhydride (PIBSA) has been analyzed using negative ion electrospray ionization mass spectrometry (ESI-MS). This mild technique gives the molecular ion distribution for the PIBSA mono-succinic acid polymer as the major product. Unexpectedly, small amounts of the PIBSA bis-succinic acid polymer were also observed. This can form a basis for a method to determine the succinic ratio of samples of PIBSA. Commercially available samples of PIBSA made from BF_3-catalyzed poly(isobutylene) and $AlCl_3$-catalyzed poly(isobutylene) were compared. While the PIBSA made from BF_3-catalyzed poly(isobutylene) consisted of polymers separated by 56 Da, the PIBSA made from $AlCl_3$-catalyzed poly(isobutylene) consisted of polymers separated by 14 Da. We attribute this to different molecular weight distributions of the starting poly(isobutylene). Poly(isobutylene) from $AlCl_3$ catalysis is postulated to form via a mechanism that consists of carbenium ion rearrangements and β scission reactions at the active site.

Introduction

Polyisobutenylsuccinic anhydride (PIBSA) is the major raw material for the synthesis of ashless dispersants, which are an important class of lubricating oil additives.[1] PIBSA is prepared by the reaction of either BF_3-catalyzed or $AlCl_3$-catalyzed poly(isobutylene) with maleic anhydride via a thermal ene reaction[2] or via a chlorination process.[3] The reaction of BF_3-catalyzed poly(isobutylene) with maleic anhydride and a free radical initiator to form poly(isobutylene)/maleic anhydride copolymers has also been reported.[4]

The number-average molecular weight (M_n) of the poly(isobutylene), the polydispersity index (M_w/M_n where M_w is the weight-average molecular weight), and the number of anhydrides attached to the poly(isobutylene) (referred to as the succinic ratio) are important factors that may influence the performance of PIBSA derivatives in fuel and lubricating oil applications.[5]

Previously, the ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra have been reported for polyisobutenyl mono- and bis-succinic anhydrides.[6] Thermal PIBSA from both $AlCl_3$-catalyzed poly(isobutylene) and from BF_3-catalyzed poly(isobutylene) have been made commercially.

We now report the negative ion electrospray ionization mass spectrum (ESI-MS) of PIBSA. This mild technique,[7] which often gives the molecular ion of high molecular weight species with little if any fragmentation, provided important information for a more complete characterization of PIBSA. Using ESI-MS, the formation of both polyisobutenyl mono- and bis-succinic anhydrides has been observed. The negative ion ESI-MS can form the basis of determining the succinic ratio of PIBSA samples. Comparison of the negative ion ESI-MS of PIBSA made from BF_3-catalyzed poly(isobutylene)[8] with PIBSA made from $AlCl_3$-catalyzed poly(isobutylene) also shows some important differences in the molecular weight distribution. These differences can be used to better understand the polymerization reaction of isobutylene to form poly(isobutylene).

Experimental Section

Commercial samples of thermal PIBSA made from 1000 molecular weight BF_3-catalyzed poly(isobutylene), OLOA 15500, and thermal PIBSA made from 1000 molecular weight $AlCl_3$-catalyzed poly(isobutylene), OLOA 2564B, were obtained from Chevron Oronite Co. LLC. These samples were used as received. A sample of OLOA 15500, prepared without diluent oil, was also received from Chevron Oronite Co. LLC.[9] Samples of low molecular weight poly(isobutylene) distillate from $AlCl_3$-catalyzed poly(isobutylene) were obtained from Paramins Co.

To prepare the dicarboxylic acid for the negative ion ESI-MS experiment, the PIBSA samples (0.1 mg) were dissolved in 3 mL of tetrahydrofuran (THF) and diluted with 1 mL of water. The addition of 1 drop of ammonium hydroxide to the dicarboxylic acid solution often resulted in the generation of greater quantities of the corresponding anion than when ammonium hydroxide was absent. In addition, larger amounts of the dianion were also observed. To prepare the amide carboxylic acid, the PIBSA samples (0.1 mg) were dissolved in methylene chloride and treated with 1 drop of ammonium hydroxide followed by dilution with a mixture of methanol/water. To prepare the ester carboxylic acid, the PIBSA samples (0.1 mg) were dissolved in methylene chloride and treated with methanol or ethanol. The preferred method for the generation of negative ions for the ESI-MS experiment is to dissolve the PIBSA in THF and dilute with water. This minimizes the formation of multiply charged ions and gives mass spectra that are easier to interpret.

The mass spectrometer was a Finnigan TSQ7000. The samples were introduced into the mass spectrometer via a syringe pump at 8 μL/min. The mass spectrometer was scanned from 10 to 2000 amu in 2 s. Almost all of the spectra were acquired in profile mode and were the result of spectra accumulation for 2 min.

The daughter ion spectra were obtained by selecting the parent ion using the first set of quadrupoles. The collision took place in the second set of quadrupoles with argon gas. The daughter ion spectra were collected by the third set of quadrupoles. The voltage offset of the second quadrupoles determined the collision energy.

GPC analysis was carried out using three PLgel columns, 5 μm, 1000 Å, 300 × 7.5 mm (Polymer Labs), using THF as solvent, 1.0 mL/min at room temperature. The sample was detected using a refractive index detector (Optilab DSP,

10.1021/ma011799h CCC: $22.00
Published on Web 02/28/2002

available from Wyatt Technology Co.), and the molar mass was measured using a multiple-angle light scattering detector (miniDAWN available from Wyatt Technology Co.). This technology determines accurate molecular weight distributions without using calibration standards.[10] The processing parameters that were used for the molar mass calculation included an exponential first-order molar mass fit and a zero detector fit degree. The calculation method included using a measured AUX calibration constant for the refraactive index detector and assumed 100% mass recovery. The total injected mass was 4.264×10^{-3} g, and the refractive index increment (dn/dc) was calculated to be 0.098.

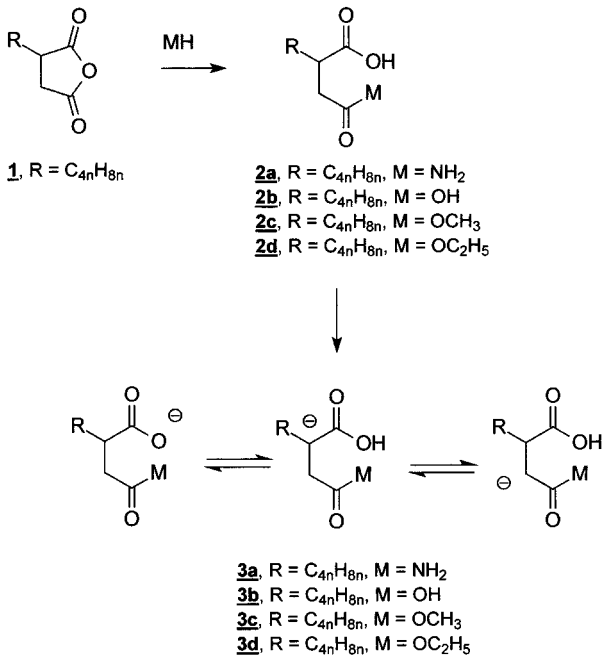
A sample of OLOA 15500 without diluent oil prepared from poly(isobutylene) with M_n of 1080 and M_w of 1760, which had a saponification number of 122.4 mg KOH/g sample and 92.8% actives (19.11 g, 0.0208 mol), was mixed with 5 mL of methanol, and this was stirred at room temperature for 24 h. The disappearance of the anhydride band at 1787 cm^{-1} was followed by FTIR. The FTIR was obtained on a Nicolet 510 FT-IR spectrometer. The sample was spotted on a salt plate (NaCl). Then the excess methanol was removed in vacuo. A total of 19.18 g of product was obtained. To 7.15 g of this product, dissolved in diethyl ether (75 mL), was then added 1-methyl-3-nitro-1-nitrosoguanidine (5.25 g, 0.036 mol). After cooling to 0 °C a solution of potassium hydroxide (1.6 g, 0.029 mol) dissolved in water (20 mL) was added. This was stirred for 1 h at room temperature. The two layers were separated, and the ether was removed using a stream of dry nitrogen. The resulting product was dissolved in hexane and filtered using a sintered glass funnel. Last, the hexane was removed in vacuo to give 7.81 g of crude ester product. This product was characterized by a FTIR ester peak at 1740 cm^{-1}. The crude ester product, 7.81 g, was dissolved in hexane and carefully placed on the top of a column of 130 g of silica gel suspended in hexane. The column was first eluted with 1 L of hexane to remove any unreacted poly(isobutylene). After removing the hexane in vacuo, we obtained 0.50 g of poly(isobutylene). Then the column was eluted with 1 L of a mixture of 50% ethyl ether and 50% hexane to recover the methyl ester of OLOA 15500. The ether and hexane were removed in vacuo to give 6.01 g of methyl ester product (77% mass recovery). The total mass recovery from this experiment was 6.51 g, 83% recovery. The ester product was characterized as follows: FTIR (salt plate) 1743 cm^{-1} (ester). ^{1}H NMR (300 MHz, $CDCl_3$): 4.7−5.4 ppm (double bond protons), 3.67−3.68 ppm (CH_3OCO protons), 1.41 ppm (CH_2 polymer chain), 1.11 ppm (CH_3 polymer chain). ^{13}C NMR (75 MHz, $CDCl_3$, 0.05 M $Cr(acac)_3$): 171−175.5 ppm (methyl ester carbon), 116−144 ppm (olefin carbons), 59.4 ppm (CH_2 polymer chain), 51.5−52.0 ppm (ester carbons), 38.0 ppm (quarternary carbon polymer chain), 31.17 ppm (CH_3 polymer chain). The analytical data indicated that the ester product was a complex mixture of double bond isomers.[11] GPC analysis of the product gave a $M_n = 1474$ and a $M_w = 2196$.

Results and Discussion

Formation of PIBSA Ions. The general reaction of an alkyl-substituted succinic anhydride (**1**), where R is an alkyl group, with ammonium hydroxide to form the amide carboxylic acid (**2a**), water to form the dicarboxylic acid (**2b**), or an alcohol to form the ester carboxylic acid (**2c** and **2d**) is shown in Scheme 1. Ionization of the carboxylic acid group or the acidic proton α to the carboxyl group provided the negative ions (**3a**−**3d**).

PIBSA Made from BF_3-Catalyzed Poly(isobutylene). PIBSA made from the thermal ene reaction of maleic anhydride with poly(isobutylene) has the general structure **(1)** where R is the polyisobutenyl group $C_{4n}H_{8n}$.[12] The location of the double bond in the R group in PIBSA depends on the structure of the poly(isobutylene) used in the preparation. For example, PIBSA made from BF_3-catalyzed poly(isobutylene)[8] is reported

Scheme 1. Generalized Reaction Scheme for the Preparation of Anions from the Reaction of PIBSA with Ammonia, Water, Methanol, and Ethanol



to be a mixture of two double-bond structures differing in the location of the double bond.[6]

The negative ion ESI-MS for the OLOA 15500 dicarboxylic acid (**3b**, R = $C_{4n}H_{8n}$) generated using THF and water is shown in Figure 1. One attractive feature of negative ion ESI-MS is that only compounds that can accommodate a negative charge are detected; diluent oil and unreacted poly(isobutylene) are not observed.

The ESI-MS shows that OLOA 15500 is a mixture of polymers with the major molecular ions at m/z = 339, 395, 451, etc., separated by 56 Da. The mixture is formed by the reaction of each poly(isobutylene) molecule m/z = 224, 280, 336, etc., in the poly(isobutylene) polymer mixture with maleic anhydride. The polyisobutenylsuccinic anhydride **1** (R = $C_{4n}H_{8n}$) is then hydrolyzed with water to form the dicarboxylic acid **2b** (R = $C_{4n}H_{8n}$), which loses a proton to give the negative ion **3b** (R = $C_{4n}H_{8n}$).

Similarly, the negative ion ESI-MS of the amide carboxylic acid (**3a**, R = $C_{4n}H_{8n}$), and the ester carboxylic acids (**3c** and **3d**, R = $C_{4n}H_{8n}$) made from OLOA 15500, gave the molecular ion expected for the corresponding structures.

The ESI-MS of the OLOA 15500 derivatives show that PIBSA consists of a mixture of polymers, each of which have a molar mass that is 98 higher than the molar mass of the starting poly(isobutylene). The ESI-MS information can in principle be used to calculate the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polydispersity index (M_w/M_n) of the PIBSA mixture. This was not done in this study, however, because the molecular weight distribution of the poly(isobutylene) that was used to make the PIBSA contained polymers up to about 10 000 molecular weight. This range extended much higher than the 2000 m/z limit of the ESI-MS experiment.

Another problem with using the ESI-MS for calculating the molecular weight distribution of the PIBSA is the fact that the ESI-MS experiment appears to be selective toward the low molecular weight ions. Pre-

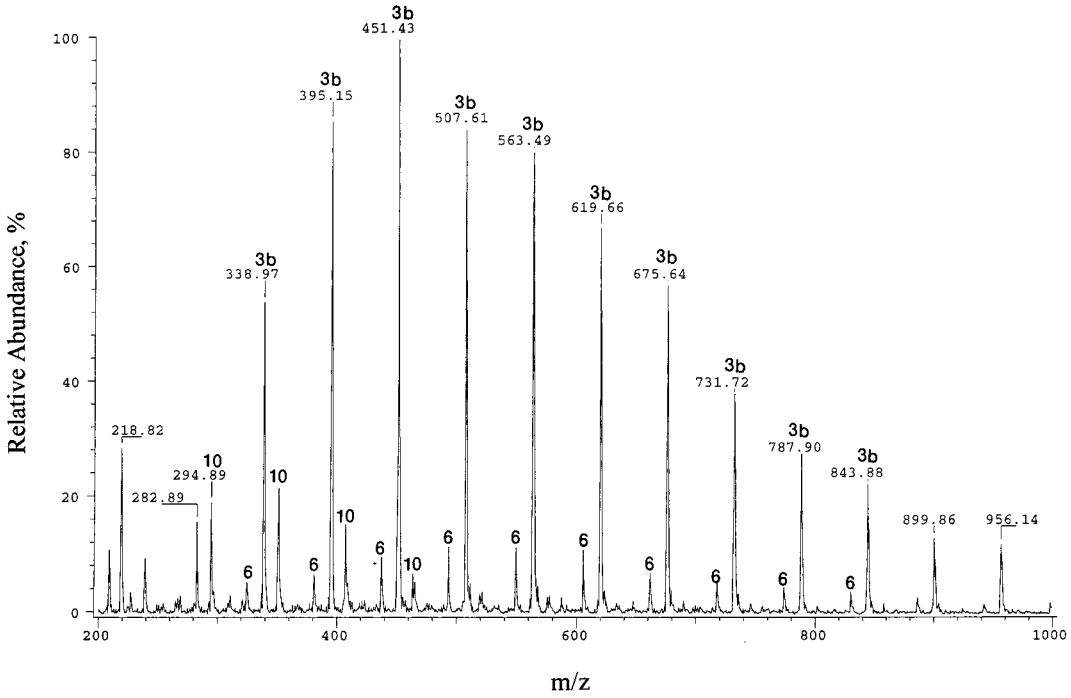


Figure 1. Negative ion ESI-MS of OLOA 15500 prepared from BF_3-catalyzed poly(isobutylene).

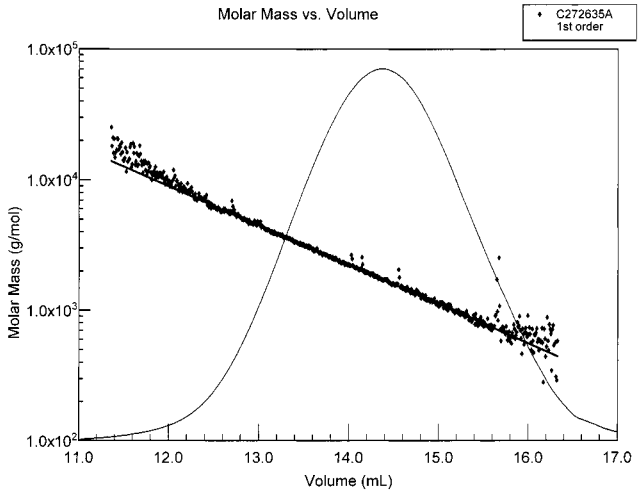


Figure 2. GPC/MALS analysis of OLOA 15500 methyl ester; M_n = 1474, pdi = 1.49.

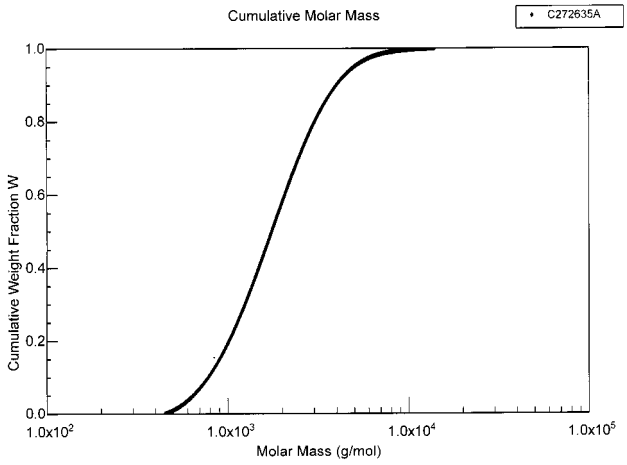


Figure 3. GPC/MALS cumulative molar mass distribution of OLOA 15500 methyl ester.

liminary experiments seem to indicate that the ionization efficiency is a function of charge density. Since these are all singly charged compounds, the higher molecular weight ones have lower charge density and therefore a decreased ionization efficiency.

To obtain the molecular weight distribution of PIBSA, we first prepared the methyl ester by reaction of the PIBSA first with methanol, followed by reaction with diazomethane. After column chromatography to remove any unreacted poly(isobutylene), the pure PIBSA ester was analyzed by GPC. The GPC trace along with the molar mass measured using a Wyatt Technology miniDAWN light scattering detector is shown in Figure 2.

The GPC analysis gave a number-average molecular weight (M_n) of 1474 for the PIBSA methyl ester. This is within the expected accuracy of this method for a PIBSA methyl ester made from poly(isobutylene) with M_n = 1080. A plot of the cumulative molecular weight is shown in Figure 3.

Close examination of the ESI-MS of the OLOA 15500 dicarboxylic acid indicated the presence of small amounts of other structures in addition to **3b** (R = $C_{4n}H_{8n}$). These are summarized in Scheme 2 and Table 2. We observed that small amounts of structure **4**, the mono-anhydride, sometime were present. In addition structures **6** and **8**, which are the derivatives of the bis-anhydride where two anhydrides have attached to each poly(isobutylene) tail, were observed. The bis-anhydride with two anhydrides attached to the poly(isobutylene) has previously been reported.[6]

Structures **5**, **7**, and **9**, which are the dianion of the mono-anhydride, the dianion of the bis-anhydride dicarboxylic acid, and the dianion of the tetracarboxylic acid, respectively, can be observed. The intensity of these structures can sometimes be increased if a base such as NH_4OH or NaOH is added to the PIBSA diacid. Assignment of **5**, **7**, and **9** as dianions is supported by the presence of ^{13}C isotope peaks located at about +0.5 *m/z* from the molecular ion in the ESI-MS.

In all of the structures **6**−**9**, the alkyl group is drawn as a single double-bond isomer. More likely, we believe

Scheme 2. Structure Assignment of Minor Components Observed in the Negative Ion ESI-MS of PIBSA

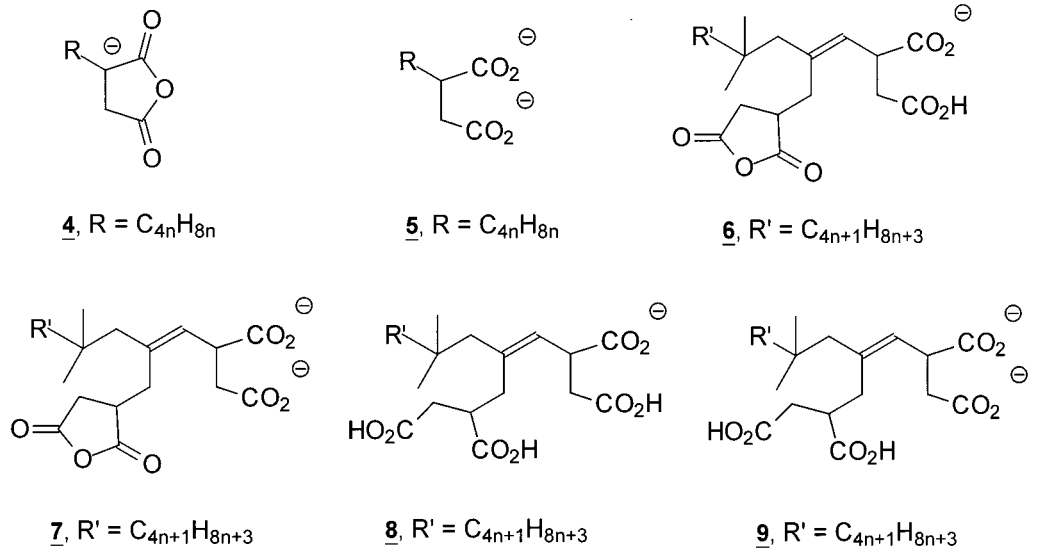


Table 1. Major Molecular Ions from the Negative Ion ESI-MS of OLOA 15500

	molecular mass (*m/z*)			
n in $C_{4n}H_{8n}$	poly(isobutylene)	**1**	**2b**	**3b**
2	112	210	228	227
3	168	266	284	283
4	224	322	340	339
5	280	378	396	395
6	336	434	452	451
7	392	490	508	507
8	448	546	564	563
9	504	602	620	619

Table 2. Assignment of Minor Negative Ion Isomers from ESI-MS of OLOA 15500

	molecular mass (*m/z*)						
$C_{4n}H_{8n}$	**4**	**3b**	**5**	**6**	**7**	**8**	**9**
112	209	227	113	325	162	343	171
168	265	283	141	381	190	399	199
224	321	339	169	437	218	455	227
280	377	395	197	493	246	511	255
336	433	451	225	549	274	567	283
392	489	507	253	605	302	623	311
448	546	564	281	662	330	680	339
505	602	620	309	718	358	736	367
561	658	676	337	774	386	792	395
617	714	732	365	830	414	848	423
673	770	788	393	886	442	904	451

that a mixture of double-bond isomers is present as shown in ref 6. Additional characterization for structures **6**−**9** has not been carried out. The R′ group in structures **6**−**9** represents the $C_{4n+1}H_{8n+3}$ group.

A fragment ion **10** was sometimes observed at *m/z* 183, 239, 295, 351, etc., due to the loss of CO_2 from **3b** (R = $C_{4n}H_{8n}$). This facile fragmentation pattern has been reported[13] for the reaction of carboxylic acids in general in the mass spectrometer, and support for this is reported below under the daughter ion section.

It is possible to use the ESI-MS intensity data and the peak assignments in Table 2 to determine the succinic ratio of PIBSA. The succinic ratio is defined as the number of anhydride groups per poly(isobutylene) tail.[14]

Close examination of the negative ion ESI-MS of the amide carboxylic acid (**3a**, R = $C_{4n}H_{8n}$) and the ester carboxylic acids (**3c** and **3d**, R = $C_{4n}H_{8n}$) from OLOA 15500 reveals similar peaks due to corresponding bisanhydrides and dicarboxylic acids of the corresponding amide carboxylates and ester carboxylates.

Table 3. Daughter Ions for PIBSA Dicarboxylic Acid (3b, R = $C_{4n}H_{8n}$)

molecular ion	energy (eV)	*m/z*	int	assignt
451	30	451	100	M^-
		407	36	$M^- - CO_2$
	40	451	68	M^-
		407	100	$M^- - CO_2$
	50	451	56	M^-
		407	100	$M^- - CO_2$

Daughter Ions of PIBSA. Collision-induced fragmentation of the molecular ions have been carried out for the PIBSA dicarboxylic acid (**3b**, R = $C_{4n}H_{8n}$), the PIBSA amide carboxylic acid (**3a**, R = $C_{4n}H_{8n}$), and the PIBSA methyl ester carboxylic acid (**3c**, R = $C_{4n}H_{8n}$). The data for PIBSA dicarboxylic acid (**3b**, R = $C_{4n}H_{8n}$) are summarized in Table 3.

As expected,[13] the major fragmentation for the PIBSA dicarboxylic acid is loss of CO_2 ($M^- - 44$). The relative amount of M^- and $M^- - 44$ is dependent on the collision energy.

Similar studies were carried out for the PIBSA amide carboxylic acid (**3a**) where the major fragmentations at 40 eV were loss of H_2O ($M^- - 18$, intensity = 10) and loss of CO_2 ($M^- - 44$, intensity = 28). For the methyl ester carboxylic acid (**3c**) the major fragmentations at 40 eV were loss of CH_3OH ($M^- - 32$, intensity = 100), loss of CO_2 ($M^- - 44$, intensity = 44), loss of CO_2 and CH_3OH ($M^- - 76$, intensity = 94), and loss of CO_2 and HCO_2CH_3 ($M^- - 104$, intensity = 12). These results are consistent with those reported earlier for dimethyl succinate.[15]

PIBSA Made from $AlCl_3$-Catalyzed Poly(isobutylene). The negative ion ESI-MS of OLOA 2564B dicarboxylic acid made from $AlCl_3$-catalyzed poly(isobutylene) is shown in Figure 4. Surprisingly, the PIBSA polymers from $AlCl_3$-catalyzed poly(isobutylene) were not separated by 56 *m/z*, but by 14 *m/z*. We hypothesize that this difference is due to the structure of poly(isobutylene) that was used to make the PIBSA. In other words, the reason the PIBSA polymers made from $AlCl_3$-catalyzed poly(isobutylene) are separated by 14 Da is

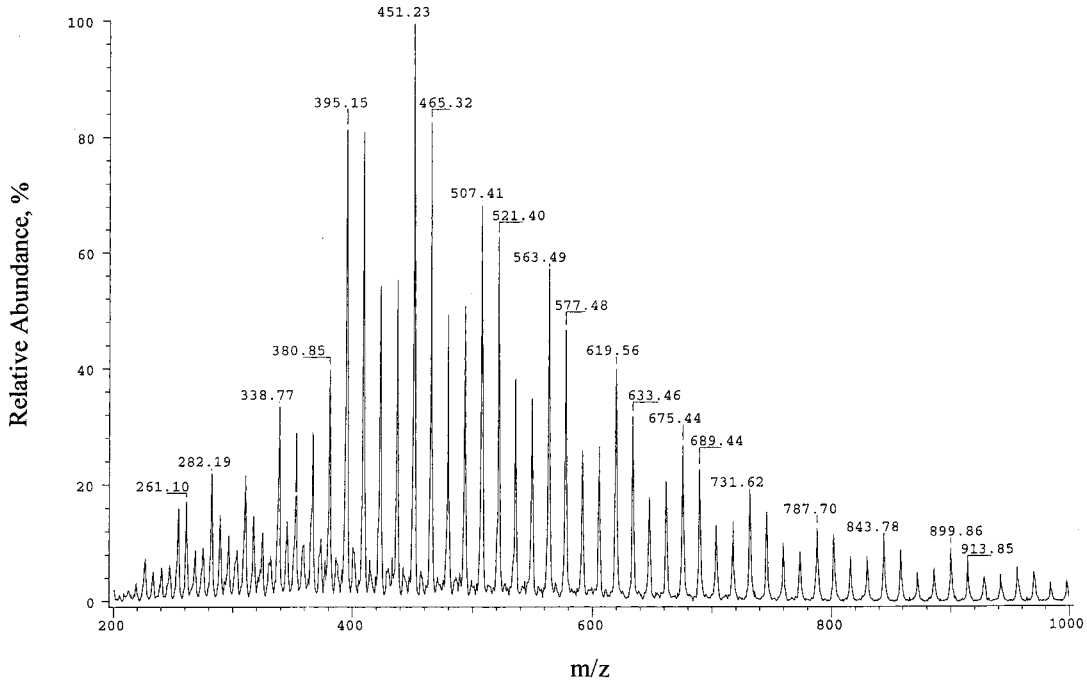


Figure 4. Negative ion ESI-MS of OLOA 2564B prepared from $AlCl_3$-catalyzed poly(isobutylene).

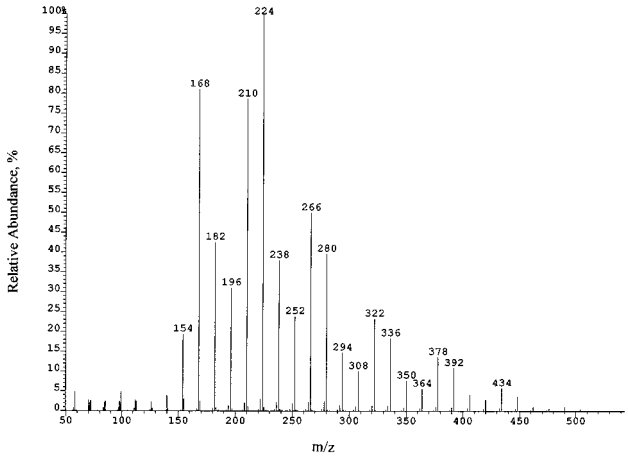


Figure 5. FIMS of $AlCl_3$-catalyzed poly(isobutylene) distillate.

because the $AlCl_3$-catalyzed poly(isobutylene) contains polymers that are separated by 14 Da. This result is surprising because ref 16, which assigned a structure to the major isomer of $AlCl_3$-catalyzed poly(isobutylene) using NMR techniques, saw no evidence to postulate anomalous carbon numbers for $AlCl_3$-catalyzed poly(isobutylene).

The ESI-MS shown in Figure 4 also shows dianions in the region of 200−400 *m*/*z* which are separated by 7 *m*/*z*.

The field ionization mass spectrum (FIMS) of a low molecular weight distillate from $AlCl_3$-catalyzed poly(isobutylene) supports this view (Figure 5). Figure 5 shows that the molecular weight distribution of poly(isobutylene) distillate made using $AlCl_3$ catalysis consists of oligomers separated by CH_2 units (14 Da). In 1984, Puskas[17] first reported the formation of products of anomalous carbon number from the cationic polymerization of poly(isobutylene).

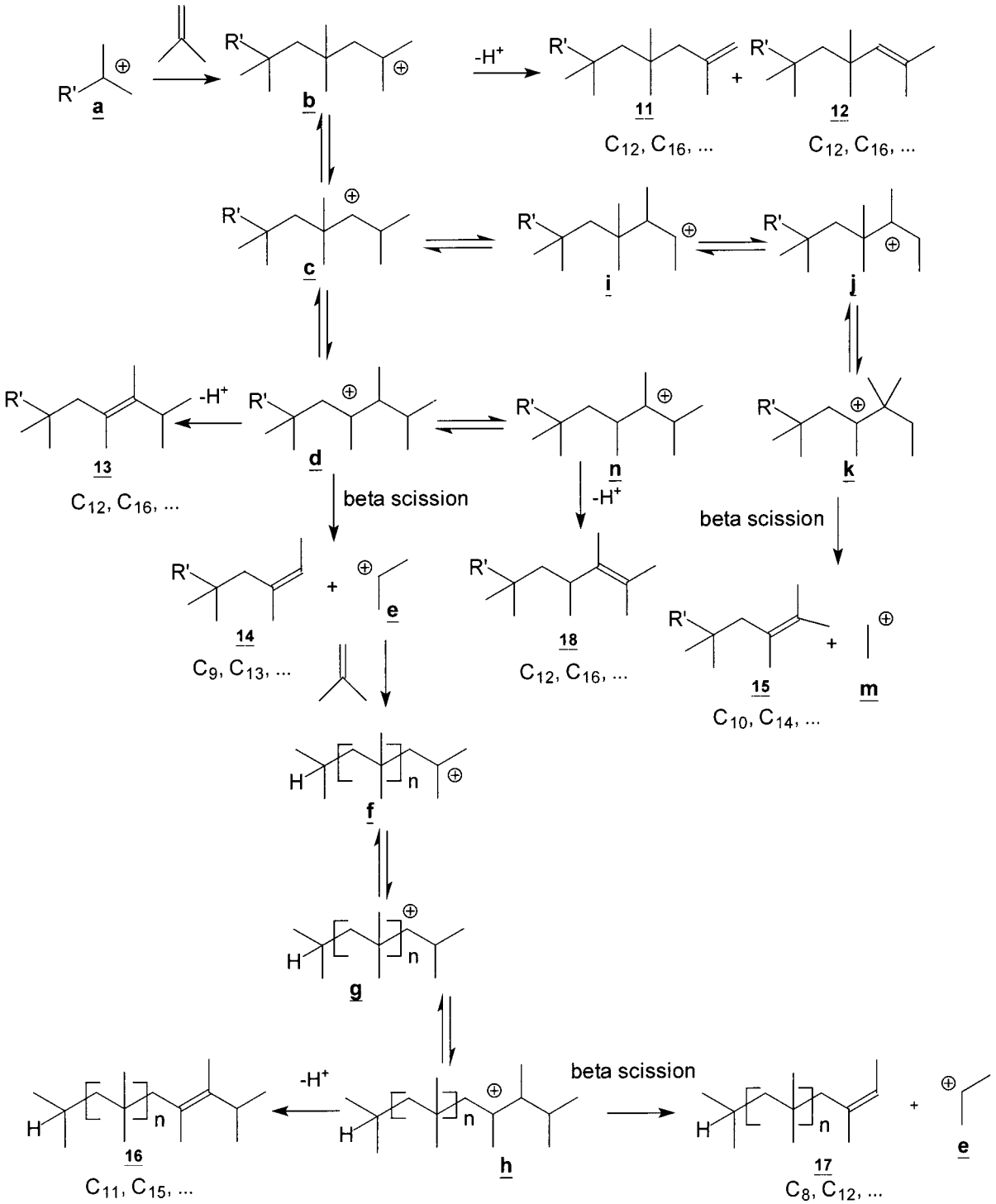
Mechanistic Considerations. This polymerization of isobutylene via BF_3 and $AlCl_3$ catalysis can be rationalized via the reactions shown in Scheme 3. Much of Scheme 3 is similar to the mechanism published in ref 18. However, Scheme 3 introduces the β scission reaction to account for the molecular weight distribution that was observed for $AlCl_3$-catalyzed poly(isobutylene). In Scheme 3, R′ equals the $C_{4n+1}H_{8n+3}$ group.

In Scheme 3 we postulate that the BF_3-catalyzed polymerization proceeds through the carbenium ion **b** to give two $C_{12,}$ C_{16}, etc., polymers **11** and **12**.

In contrast, a mechanism for the $AlCl_3$-catalyzed polymerization of isobutylene must account for the presence of C_9, C_{13}, etc., C_{10}, C_{14}, etc., and C_{11}, C_{15}, etc., polymers. The $AlCl_3$ polymerization can proceed via a carbocation rearrangement (**b** to **c** to **d**) to give the C_{12}, C_{16}, etc., polymer **13**, or via a β scission reaction from **d** to give a C_9, C_{13}, etc., polymer **14**, and the C_3H_7 carbocation **e**. Storey[19] has recently emphasized the importance of carbocation rearrangements in controlled/living isobutylene polymerization. The C_3H_7 carbocation **e** can then initiate the formation of another poly(isobutylene) polymer by reaction with isobutylene. The C_3H_7 initiated poly(isobutylene) carbenium ion (**f**) can rearrange (**f** to **g** to **h**) to form **16**, the C_{11}, C_{15}, etc., polymer, or can undergo a β scission reaction from **h** to give **17**, a C_8, C_{12}, etc., polymer. Likewise, carbenium ion **d** could undergo rearrangement to **n** to form **18**.

To generate poly(isobutylene) which contain the C_{10}, C_{14}, etc., repeat unit, a mechanism that generates a C_2 (or a C_6 or higher) fragment is necessary. We propose that the carbenium ion **c** undergoes a rearrangements (**c** to **i** to **j** to **k**) followed by β scission to form the C_{10}, C_{14}, etc., polymer **15**, and the C_2H_5 carbocation **m**. The high-energy C_2H_5 cation **m** could also initiate the formation of another poly(isobutylene) polymer by reaction with isobutylene. Evidence for the presence of a terminal ethyl end group in $AlCl_3$ catalyzed poly(isobutylene) has already been reported.[16] However, the energetics of generation of the relatively high energy primary C_2H_5 cation from a more stable tertiary carbocation might make this pathway less likely.[20] Examination of the intensities of the ESI-MS for the poly(isobutylene) C_{10}, C_{14}, etc., polymer **15**, indicates that this is the least likely pathway. The pathway that

Scheme 3. Proposed Reaction Scheme To Explain the Molecular Weight Distribution of $AlCl_3$-Catalyzed Poly(isobutylene) ($R' = C_{4n+1}H_{8n+3}$) Involving Carbenium Ion Rearrangements and β Scission Reactions in the Polymerization of Isobutylene



generated the poly(isobutylene) C_{12}, C_{16}, etc., polymer (**11**, **12**, **13**, and **17**) had the highest frequency of occurrence.

The importance of 1-butene and 2-butene, which are normally present in small amounts in the isobutylene feed, may also play a role in the detailed understanding of the polymerization mechanism.

The β scission reactions of a tertiary carbenium ion to a primary carbenium ion occur in the acid-catalyzed cracking of olefins at elevated temperatures.[21] Quantum mechanical calculations on the mechanism of the β scission reaction on zeolite catalysts have been performed.[22] These studies have shown that the potential energy surface for this reaction is very complex. Three possible reaction paths were located. A two-step path via a hydrogen-bonded transition state and a substituted cyclopropane had the lowest activation barrier.

The mechanism in Scheme 3 is supported by the observation of both *tert*-butyl and isopropyl end groups in $AlCl_3$-catalyzed poly(isobutylene).[16] In addition, the major olefin end groups for $AlCl_3$-catalyzed poly(isobutylene), which was a trisubstituted olefin group,[16] is

supported by isomers **14** and **17**. Interestingly, in contrast to ref 16, Scheme 3 predicts that the trisubstituted olefin end group appears with both the isopropyl group (**17**) and *tert*-butyl group (**14**) at the other end of the poly(isobutylene). The presence of the tetrasubstituted olefin end groups in structures **13**, **16**, and **18** has been proposed for $AlCl_3$-catalyzed poly(isobutylene) as well.[23] The postulated tetrasubstituted end group in structure **15** has not yet been reported, however.

An in-depth study of the energetics of the mechanism for the polymerization of isobutylene would be of considerable interest.

Conclusions

The negative ion ESI-MS of PIBSA is reported for the first time. The ESI-MS of PIBSA made from BF_3-catalyzed poly(isobutylene) shows that PIBSA is a mixture of polymers that differ in molecular weight by 56 Da. Each polymer in the mixture is the reaction product of poly(isobutylene) with maleic anhydride. The ESI-MS of PIBSA shows the presence of both polyisobutenyl mono and bis succinic anhydrides. The ESI-MS can be used as the basis for a method to measure the succinic ratio of PIBSA.

The collision-induced fragmentation of PIBSA dicarboxylic acid, amide carboxylate, and ester carboxylate was also studied. The primary fragmentation pathway was the loss of CO_2.

In contrast, the negative ion ESI-MS of PIBSA made from $AlCl_3$-catalyzed poly(isobutylene) shows that PIBSA is a mixture of polymers that differ in molecular weight by 14 Da. We have proposed that this difference is due to a difference in the $AlCl_3$-catalyzed poly(isobutylene). The $AlCl_3$-catalyzed poly(isobutylene) may undergo carbenium ion rearrangements and a β scission reactions to generate C_9, C_{13}, etc., C_{10}, C_{14}, etc., and C_{11}, C_{15}, etc., polymers.

References and Notes

(1) Liston, T. V. *Lubr. Eng.* **1992**, 389.
(2) Anderson, R. G.; Stuart, F. A.; Drummond, A. Y. US Patent 3,018,291, Jan 23, 1962.
(3) Weill, J.; Sillion, B. *Rev. Inst. Fr. Pet.* **1985**, *40* (1), 77.
(4) Harrison, J. J. US Patent 5,112,507, May 12, 1992.
(5) Hancsok, J.; Bartha, L.; Baladincz, J.; Kocsis, Z. *Lubr. Sci.* 11−3, May **1999** (*11*), 297.
(6) Tessier, M.; Marechal, E. *Eur. Polym. J.* **1984**, *20* (3), 269.
(7) Gaskell, S. J. *J. Mass Spectrom.* **1997**, *32*, 677.
(8) Mach, H.; Rath, P. *Lubr. Sci.* 11−2, February **1999** (*11*), 175.
(9) We would like to thank W. R. Ruhe and S. J. Willis for providing a sample of this material.
(10) Wyatt, P. J. *Anal. Chim. Acta* **1993**, *272*, 1.
(11) A more detailed peak assignment of the ^1H and ^{13}C NMR spectrum of polyisobutenylsuccinic esters will be the subject of a future paper.
(12) The negative ion ESI-MS experiment is not capable of distinguishing between double-bond isomers with the same molar mass. For this reason we prefer not to show the position of the double bond in the R group of the PIBSA.
(13) Bowie, J. H. *Mass Spectrom. Rev.* **1990**, *9*, 349.
(14) We are developing a method to calculate the succinic ratio of PIBSA based on the ESI-MS.
(15) Raftery, M. J.; Bowie, J. H. *Aust. J. Chem.* **1987**, *40*, 711.
(16) Harrison, J. J.; Young, D. C.; Mayne, C. L. *J. Org. Chem.* **1997**, *62*, 693.
(17) Puskas, I.; Meyerson, S. *J. Org. Chem.* **1984**, *49*, 258.
(18) Gunther, W.; Maenz, K.; Stadermann, D. *Angew. Makromol. Chem.* **1996**, *234*, 71.
(19) Storey, R. F.; Curry, C. L.; Brister, L. B. *Macromolecules* **1998**, *31*, 1058.
(20) A referee has suggested that in accordance with literature data on 2-methylbutene-2, structure 14 is expected to add more isobutene. By repeating the same β scission mechanism as proposed for structure 14, homologue series of C10, 14, 18, etc., would result.
(21) Buchanan, J. S.; Santiesteban, J. G.; Haag, W. O. *J. Catal.* **1996**, *158*, 279.
(22) Frash, M. V.; Kazansky, V. B.; Rigby, A. M.; van Santen, R. A. *J. Phys. Chem. B* **1998**, *102*, 2232.
(23) Argo, C.; Gillam, S. M.; Orsini, F. *Polym. Bull. (Berlin)* **2000**, *44*, 71.

MA011799H