Microstructure and Composition of Ethylene−Carbon Monoxide Copolymers by Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry

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ABSTRACT: Low molecular weight ethylene/carbon monoxide (E/CO) copolymers were characterized by matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. Because of the nominal mass overlap between ethylene and carbon monoxide monomers, the normal copolymer oligomer distribution cannot be observed by time-of-flight (TOF) mass analysis, and no composition or microstructure information can be obtained. Chemical reduction of the carbon monoxide to a hydroxyl permits observation of an ECO copolymer distribution by increasing the mass of each oligomer in proportion to the carbon monoxide content. Unfortunately, the poor ionization efficiency of the fully reduced copolymer precludes quantitative composition and microstructure measurements. MALDI in combination with Fourier transform−ion cyclotron resonance (FT-ICR) mass spectrometry permits oligomers having the same total number of monomers but different amounts of ethylene and carbon monoxide to be mass resolved. The discrete oligomer distribution obtained by MALDI-FT-ICR allows E/CO composition and microstructure to be determined. A first-order Markovian model was fit to the experimental data. Oligomers were found to have an alternating sequence of single carbon monoxide monomers between longer lengths of ethylene monomers.

Introduction

The analysis of synthetic polymers by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) has become a popular method in recent years. Using the proper experimental conditions, especially the choice of matrix and cationizing agent, diverse polymer types can easily and quickly be ionized to give spectra containing a distribution of intact oligomers of varying length.[1−3] This allows not only the determination of traditional parameters such as average molecular weight but also the ability to examine the structure of individual oligomers, something usually impossible by methods such as gel permeation chromatography (GPC). In a similar fashion, copolymers can be analyzed by MALDI-MS to give distributions of oligomers at each length of different monomer ratios, from which the additional information on composition and sequence can be extracted.[4−7]

However, copolymers tend to be more experimentally challenging, as the comonomers may have disparate requirements for ionization. For example, in our experience, polyolefin copolymers are difficult to ionize by MALDI.[8] This is likely due to the high content of saturated monomers and the paucity of polar functionality for charge attachment. Not surprisingly, most polymers comprised of completely saturated olefin monomers are unable to be examined at all by MALDI-MS, as cation attachment to simple alkyl groups is not energetically favorable.[9,10] Sufficient comonomer functionality (in some cases, end-group functionality[11,12]) and/or content, though, does permit MALDI-MS analysis.

One such polyolefin copolymer that is potentially amenable to analysis by MALDI-MS is ethylene (E)−carbon monoxide (CO) copolymer (E/CO). E/CO is synthesized by both free radical and transition metal catalyzed reaction of pure feeds, or of syngas, which consists of an impure mixture of CO and H_2 in varying proportions.[13,14] Being easily photolyzed, E/CO has previously found almost exclusive application in beverage ring carriers required by law to be degradable.[15] The aforementioned difficulty in ionizing the ethylene component of E/CO notwithstanding, MALDI-MS analysis of the copolymer would seem straightforward if the oligomers could be sufficiently ionized. But because ethylene (28.031 Da) and carbon monoxide (27.995 Da) monomers have the same nominal mass, resolution of E/CO copolymer at molecular weight around 1000 Da would require a mass resolving power (RP) of 27 500. MALDI-MS spectra of the copolymer obtained by a time-of-flight (TOF) mass spectrometer with a lower RP would not be suitable for structural or compositional analysis, as oligomers of the same length but different composition occur at the same unit mass.

Although this makes routine analysis of E/CO by MALDI-MS problematic, it is not impossible. In previous related work, Simonsick and co-workers described two approaches to this problem for the MS analysis of another copolymer having different isobaric monomers, glycidyl methacrylate/butyl methacrylate. In the first, glycidyl monomers were reacted to shift oligomer peaks a given mass for each monomer in the oligomer, and the reacted products were then analyzed by laser desorption Fourier transform−ion cyclotron resonance mass spectrometry (FT-ICR MS).[16] In the second method, the oligomers were not reacted, but instead analyzed by electrospray ionization FT-ICR MS using a high magnetic field to resolve the exact mass difference

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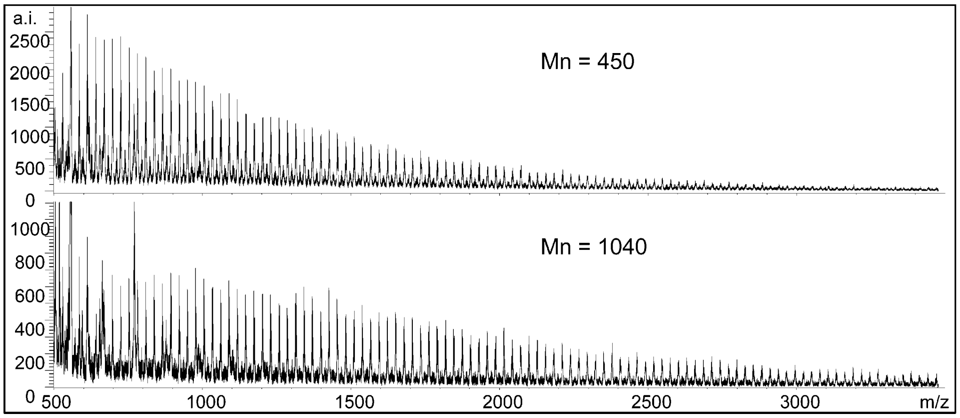

Figure 1. (top) MALDI-TOF spectrum of ECO 445 with silver cationization. (bottom) ECO 1040, with greater intensity of higher mass oligomers and broader distribution. In both cases, ions below 500 *m/z* were deflected to prevent detector saturation from matrix peaks.

(0.036 u) between the two monomers.[17] Although MALDI was not used in these cases, variations of these methods using MALDI as an ionization source may be applicable to the analysis of E/CO and, in the first case, would permit the use of the more common MALDI-TOF mass spectrometer.

Here, we explore the MALDI-MS spectra of E/CO copolymers and examine various methods for obtaining composition and microstructural information from the spectra. First, we determine optimal experimental conditions for MALDI-TOF analysis of E/CO oligomers and examine the low-resolution copolymer spectra resulting from comonomers of the same unit mass. Facile reduction of the carbon monoxide monomers to hydroxyls by chemical reaction is explored as a means to separate isobaric peaks arising from oligomers of the same length but different comonomer ratio. Both the effects of this change in functionality on the observed MALDI-TOF spectra and the utility of the spectra for composition and structural analysis are then investigated. MALDI-FT-ICR spectra of E/CO with well-resolved isobaric oligomer peaks are also examined. Finally, Bernoullian and Markovian statistical models of the FT-ICR spectra are used to determine the microstructure of the copolymer.

Experimental Section

E/CO (M_n =1040 and 445 g/mol, M_w = 1890 and 1100 g/mol as determined by GPC) copolymers containing carbon monoxide compositions of 29.2% and 18.2%, and 51 and 114 branches per 1000 carbons, respectively, as determined by NMR, were prepared via a free radical polymerization procedure similar to that described in a previous work.[14] Dithranol, indoleacrylic acid (IAA), *all-trans*-retinoic acid (RA), and silver trifluoroacetate (AgTFA) were obtained from Aldrich (Milwaukee, WI) and used without further purification. All solutions for MALDI analysis were prepared in tetrahydrofuran or toluene at a concentration of 10 mg/mL. Matrix, cation, and analyte were mixed in a volume ratio of 8:1:4, respectively, and a 1 uL aliquot of this mixture was applied to the probe tip and allowed to air-dry.

For the chemical reduction, a 10 mg/mL solution of E/CO copolymer in THF was placed in a round-bottom flask or glass vial. To this solution, a multifold molar excess of sodium borohydride or lithium aluminum hydride (Aldrich, Milwaukee, WI) was added and stirred with a magnetic bar or vortexer at room temperature. After 1 h, stirring was discontinued and the solution allowed to remain at room temperature indefinitely. Samples for MALDI analysis were taken directly from the reaction mixture after various reaction times without further purification and prepared in a similar fashion as to above.

Time-of-flight mass spectra were acquired on a Bruker (Billerica, MA) Biflex III MALDI mass spectrometer operating in reflectron mode using delayed extraction with the Scout 384 source. Ion deflection below 500 *m/z* was used to prevent matrix signal saturation and detector desensitization. Spectra were acquired with a minimum of 50 shots per spectrum, with the probe position moved slightly approximately every 5−10 shots when visible sample depletion was observed and/or when the signal decreased significantly. Calibration was performed with *p*-methylstyrene polymers of various molecular weights supplied by ExxonMobil. High-resolution broadband excitation spectra were acquired on a Bruker Apex III FT-ICR with a 12 T magnet and a SCOUT 100 MALDI source. One million data point spectra from 100 to 2000 *m/z* were obtained from an average of 300 scans, with 10 laser shots per scan, and were calibrated with internal silver cluster peaks.

For the TOF spectra, peak integration was performed using the XTOF (Bruker) software. With the FT-ICR spectra, peak identification and integration were performed using the copolymer analysis module of the Polymerix software package (Sierra Analytics, Modesto, CA). Statistical modeling was performed using programs written in the MATLAB language (Mathworks, Inc.), and data were formatted and calculations were performed in Excel (Microsoft, Redmond, WA).

Results and Discussion

MALDI−TOF Analysis. Initial efforts in characterizing the M_n = 1040 E/CO copolymer (E/CO 1040) by MALDI-TOF were unproductive. A cloudy solution was observed when preparing solutions of the copolymer at the usual concentrations for analysis in THF at room temperature, indicating incomplete solvation of the E/CO oligomers. This likely precluded detection, as complete solvation of the polymer in liquid MALDI sample preparation is critical to effective crystallization of the polymer/matrix mixture and thus desorption/ionization.[18,19] However, when hot THF was used to dissolve the sample, a clear solution was obtained, which remained clear for 1−2 days after cooling to room temperature. Using hot THF for solvation of E/CO 1040 and toluene solvent for E/CO 445, spectra were easily obtained for both with silver cationization using dithranol (Figure 1) or IAA. RA gave poor signal-to-noise ratios and was not used further. Various ratios of matrix, analyte, and salt were attempted, with the ratio of 8:4:1 found being most productive. Though a metallic salt aided ionization, it should be noted that no metal cation was required, as spectra were also obtained without the

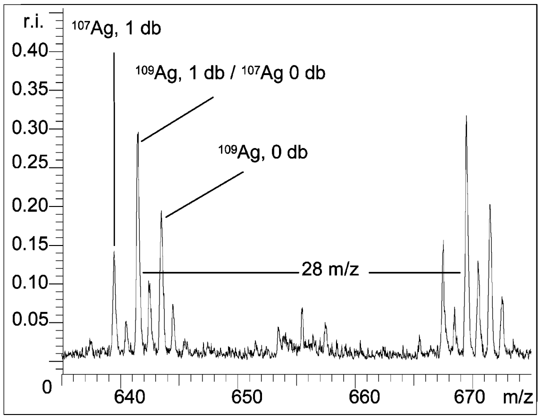

Figure 2. Expanded view of ECO 445 spectrum from Figure 1. Isotopic distributions arising from $^{107/109}$Ag and saturated/unsaturated oligomers (db = double bond) are separated by 28 m/z, equivalent to the unit mass of an ethylene or carbon monoxide monomer.

use of AgTFA (data not shown). Signal intensity was insufficient for analytical usefulness, but clusters of poorly resolved bands (4−5 m/z wide) were observed with relatively high laser power at 14 m/z spacing, indicating the signal may be due to fragmentation. Although their relative composition is small compared to that of the ethylene, the carbon monoxide monomers do permit ionization of the oligomers by silver cationization.

The wide polydispersity of the polymers (1.8−2.5 from GPC measurements) is evident in Figure 1. As shown, the peaks extend from just above 400 m/z to over 3000 m/z in the case of the E/CO 1040. The oligomer distributions of the two samples are clearly different, though ion deflection and the large polydispersity prohibit accurate calculation of the molecular weights.[20] As shown in Figure 2, single sets of peaks are observed every 28 mass units, correlating to either the addition of a carbon monoxide or an ethylene monomer. Because of the lack of a nominal mass difference between the two monomers, the spectrum looks much like that of a homopolymer. This is in contrast to spectra of other copolymers without isobaric monomers, where oligomers of different monomer content but the same length have sufficiently different masses, which enables one to easily differentiate between oligomers of different composition. The secondary peaks observed in between the primary series are 14 m/z higher, which is likely the result of an odd number of carbons in the backbone chain and/or decay of the oligomer chains.

From the masses of each peak in the spectrum, the length of each oligomer chain can be calculated. The peak at 639 m/z (Figure 2) corresponds to the oligomer that contains 19 ethylenes or carbon monoxides, and has one double bond, with a single ^{107}Ag cation. The peak two m/z higher corresponds not only to the unsaturated oligomer with a ^{109}Ag cation but also to a saturated oligomer of 19-mer length with a single ^{107}Ag cation. This is shown by the skew in the isotopic distribution, as the ^{107}Ag and ^{109}Ag peaks would be relatively equal were it not for the suspected unsaturated/saturated difference. The peak at 643 m/z corresponds to the ^{109}Ag peak of the saturated oligomer. Similar isotopic distributions are observed at other oligomer lengths throughout the spectrum.

Hydrogenation MALDI-TOF Analysis. Because of the lack of the nominal mass difference in the ethylene and carbon monoxide monomers, calculating composition from the distribution of oligomer peaks as with other copolymers is impossible. Oligomers of different composition but same number of monomers have overlapping unit masses and cannot be resolved with MALDI-TOF. The use of a reducing agent was thus explored to gain compositional information. Reducing agents such as sodium borohydride or lithium aluminum hydride are commonly used to reduce the carbon monoxide functionality, whether aldehyde or ketone, in organic compounds to a hydroxyl, and have been used in the past to reduce E/CO copolymers.[21] This reaction inserts two hydrogens for every carbon monoxide group reacted, resulting in a 2 m/z shift to higher mass. Carbon−carbon double bonds are generally unaffected. Thus, an oligomer containing five carbon monoxide groups with the same nominal mass as an oligomer with four carbon monoxide groups and an additional ethylene group would, after complete reduction, be 2 m/z higher in mass than the oligomer with four carbon monoxides. Obviously, oligomers of different monomer composition but the same total number of monomers could then in theory be easily distinguished after reduction by the change in mass.

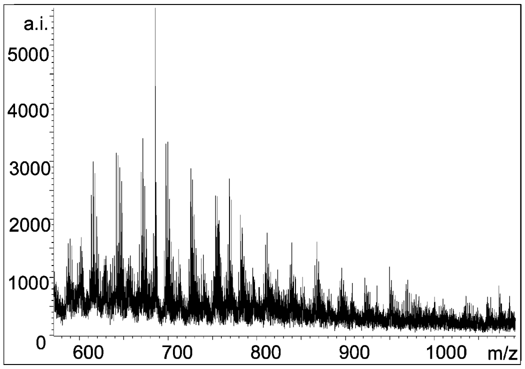

Figure 3. Reduction products of ECO 445. Note lower signal-to-noise and lack of higher mass peaks as compared to Figure 1.

To make the reduction procedure as facile and simple as possible, the reducing agent in solid form was added to the polymer solution in standard vials used for MALDI sample preparation in our laboratory, and the reacted products were analyzed directly from the reaction mixture without purification. Spectra taken immediately after addition of sodium borohydride showed no change, but at longer periods, significant changes in the spectra were noted. A typical spectrum of the reduction products of E/CO 445 after 1 week is shown in Figure 3, with silver cationization. Wider distributions in each of the peak clusters are noticeable, though the spacing between main peak groupings remains the same at 28 m/z. The higher mass oligomers, however, are not as intense as previously observed in the unreacted spectra. This may be due to either interference effects of the high concentration of sodium borohydride or the increased number of peaks for an oligomer of a given length after reaction causing saturation. Direct comparison of unreacted and reduced E/CO copolymer shows the upward mass shift after reaction (Figure 4). The main isotopic peak spacing remains at 2 m/z due to the requirement of two hydrogen additions for every carbon monoxide.

By calculating the difference in the average molecular weight for a distribution of peaks at a certain oligomer length both before and after reaction, one can obtain

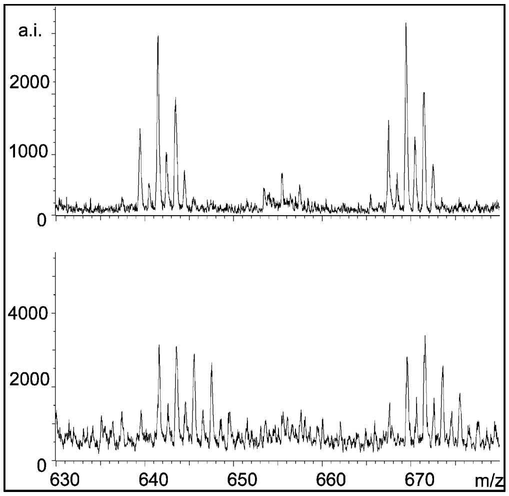

Figure 4. Comparison of reacted (bottom) and unreacted (top) ECO 445 MALDI-TOF spectra. The isotopic distributions in the reacted spectrum are shifted to higher mass due to the conversion of the oligomer carbonyls to hydroxyls.

compositional information. Assuming no preferential ionization and a complete reaction, the mass shift should be proportional to the average number of carbon monoxides in an oligomer of a certain length, as each carbon monoxide monomer that reacts will increase the mass of an oligomer by two units. For the peaks at ~641 *m*/*z* in Figure 4, the mass shift from the difference in average weight of the isotopic distribution is approximately 3 *m*/*z*, which corresponds to 1.5 carbon monoxides. Given that this is a 19-mer oligomer, the calculated composition is approximately 8 mol %. This is less than half the value determined by NMR (18.2%). Similar discrepancies are observed for oligomers of other lengths.

Clearly, the difference in composition values determined by derivitization/MALDI-TOF and NMR may be the result of an incomplete reaction. If sufficient amounts of E/CO oligomers remain unreacted, these oligomers would lower the average molecular weight calculated for each oligomer. In this case, subtraction of the unreacted oligomer contribution to the isotopic distribution of reacted oligomers should result in a higher (correct) value for the average molecular weight. This is done by normalizing the areas of the isotopes in the observed distribution for oligomers of a given length to the intensity of the first isotope of the distribution of same length in the reacted sample and then subtracting the normalized areas from the values for the reacted oligomer isotopic distribution. However, the effect of the unreacted oligomers is only minor, as the average molecular weight of the reacted products after subtraction is only 0.5 *m*/*z* higher than the previous value, resulting in only a minor increase of calculated composition to ~9%. This is again is less than half of the composition as determined by NMR.

Still, incomplete reaction may be causing the discrepancy in composition, as the above procedure for correcting for unreacted oligomers is crude. However, at longer reaction times, signal decreased rapidly until no E/CO oligomers could be observed in the MALDI-TOF spectra. Analysis of the reaction mixture using infrared spectroscopy showed nearly complete absence of the purported carbon monoxide peak dominant in infrared spectra of the unreacted sample and the presence of a broad, strong absorption in the region associated with the hydroxyl functionality (data not shown). Similarly, when a stronger reducing agent, lithium aluminum hydride, was used in place of sodium borohydride, no MALDI-TOF signal could be observed, even immediately after addition of the reducing agent.

Because the MALDI-TOF signal disappeared both at extended reaction times and with a stronger reducing agent, the complete conversion of the carbon monoxide to hydroxyl was confirmed by infrared analysis, and subtraction of unreacted peaks did not effect the composition value; it is likely that the discrepancy in composition values is attributable to ionization biases. Oligomers with few or no carbon monoxide groups and/or more hydroxyl groups may not cationize well with silver and may have significantly different requirements for efficient MALDI. To test this, a fully hydrolyzed (99.2%) low molecular weight ($D_p = 50-100$) commercial poly(vinyl alcohol) (PVOH) was obtained (OKS-9018N, Nippon Synthetic Chemical Industry Co., Osaka, Japan). This sample effectively mimics a fully reduced E/CO copolymer with high carbon monoxide content. Using a similar sample preparation as for the reaction mixture, no MALDI-TOF signal attributable to the polymer could be observed. Because the PVOH was not fully solvated in THF, giving a cloudy solution, the aforementioned difficulties with solubility and effective detection by MALDI may play a role in the inability to observe the reduced oligomers, in addition to the inability to attach a silver cation to the hydroxyl functionality.

MALDI FT-ICR Analysis. Though the reduced copolymer was unable to be ionized by MALDI, ionization of the unreacted copolymer was successful, albeit with overlapping oligomers of the same nominal mass due to the relatively low resolution of the TOF instrument, even with delayed extraction and in reflector mode. With this in mind, MALDI-FT-ICR was explored because of the potentially higher resolving power of the FT-ICR mass spectrometer, especially with higher magnetic fields. MALDI-FT-ICR has been previously used to analyze triblock copolymers of poly(oxypropylene) and poly(oxyethylene),[22] but these copolymers did not have isobaric monomers as does E/CO. Although ESI-FT-ICR has been used to successfully resolve oligomers with the same with monomer mass difference as E/CO, 0.036 *m*/*z*,[18] the MALDI-FT-ICR analysis of the same copolymers has been unsuccessful, especially at higher masses.[17] The tendency of MALDI to produce singly charged ions creates a spectrum with species of higher mass-to-charge which are necessarily harder to resolve than the lower *m*/*z* multiply charged ions in ESI mass spectra. Additionally, MALDI-FT-ICR spectra can be problematic when used for the determination of the average molecular weight due to isotope beating effects[23] and molecular weight dependent trapping discrimination.[24−26] However, in the case of E/CO, the oligomers are of sufficiently low molecular weight that the singly charged ions do not present a problem, and the copolymer distributions at each oligomer length are narrow enough (<1 *m*/*z*) to preclude molecular weight discrimination effects.

Figure 5 shows a segment of the MALDI-FT-ICR spectrum of E/CO 445 with silver cationization. The spectra are similar to that obtained by TOF (Figure 2) but appear to have additional peaks at masses of 2 *m*/*z* multiples less than the peaks observed in the TOF spectrum, likely corresponding to multiple unsatura-

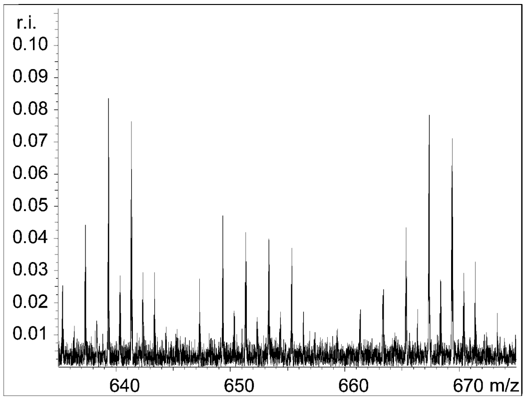

Figure 5. MALDI-FT-ICR spectrum of ECO 445 with silver cationization. Mass range is same as that in Figure 2, but resolution is increased significantly.

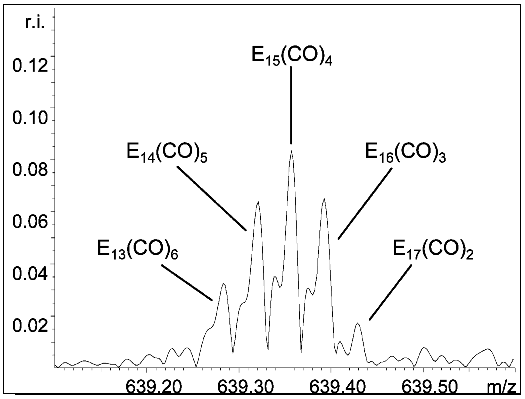

Figure 6. Expanded view of 19-mer from Figure 5 showing resolution of isobaric oligomers. Peak shoulders arise from ^{109}Ag isotopes of oligomers of the same monomer number with an additional unsaturation site (i.e., two fewer hydrogen atoms).

tions. It is possible the longer residence time in the FT-ICR permits the decay of oligomers to unsaturated, smaller length chains that are not observed in the TOF spectra. The higher intensity of the peaks separated by 14 *m*/*z* from the main series may also be the result of decay.

On close examination, each of the peaks in Figure 5 is comprised of a narrow distribution of resolved oligomer peaks, as shown in Figure 6 for the 19-mer, much like normally obtained over a broader mass range for copolymer with significant monomer mass difference. Peaks at each oligomer length up to 1000 *m*/*z* were similarly resolved. The main series of peaks in Figure 6 are separated by 0.036 *m*/*z*, equivalent to the mass difference between an ethylene and carbon monoxide, 0.036 Da, and represent oligomers of different composition (monomer ratio) but the same length. From the exact mass of a peak, the monomer ratio of each can easily be determined, as shown in Figure 6. As *m*/*z* is increased in 0.036 increments, an additional ethylene is gained at the expense of a carbon monoxide. Both the carbon monoxide composition of the copolymer and oligomer length are sufficiently high so that no oligomers with zero carbon monoxide are observed. The smaller series of peaks, which appear as shoulders, is separated by 0.016 *m*/*z* from the main series, the same as the exact mass difference between ^{109}Ag and ^{107}Ag H_2, giving additional evidence oligomers 2 *m*/*z* lower have additional unsaturation.

Composition and Microstructure. From the copolymer distribution at each oligomer length, the composition of the copolymer can be calculated. Integrated areas and composition were obtained from each of the singly unsaturated ^{107}Ag cationized oligomer peaks in the distributions at each length in the 350−1000 *m*/*z* mass range with the Polymerix software. The total composition of the copolymer was then determined by averaging the composition of each oligomer obtained by the following equation:

$$\text{mol \% CO} = \frac{\sum_{x=0}^{n} (\mathrm{CO}_x\mathrm{E}_{(n-x)})(x/n)}{\sum_{x=0}^{n} (\mathrm{CO}_x\mathrm{E}_{(n-x)})}$$

where n refers to the total number of monomers, and $\mathrm{CO}_x\mathrm{E}_{(n-x)}$ is the peak area of an unsaturated ^{107}Ag peak with n total monomers and x CO monomers. The average composition of the copolymer was found to be 21.8 ± 0.8 mol % carbonyl, based on three spectra taken from the sample spot. This is comparable, though slightly higher, to the value obtained by NMR, 18.2%. One possible explanation of this small difference could be increased ionization efficiency of oligomers with increased functionality, i.e., carbonyls. However, the composition calculation for individual oligomers between 350 and 1000 *m*/*z* showed no compositional drift with increasing oligomer length, although the scatter was greater for smaller lengths. If ionization efficiency were dependent on the absolute number of carbon monoxide monomers, the observed composition should change with oligomer length. A bias in the NMR measurement or a compositional drift for oligomer lengths higher than 1000 *m*/*z* are more plausible explanations.

Using the same copolymer oligomer distribution, statistical modeling can be used to determine not only the composition of the copolymer but also the microstructure.[27,28] Both Bernoullian and first-order Markovian statistics were used to model the copolymer distributions. In the Bernoullian model, the addition of a monomer to an oligomer chain is assumed to be independent of the preceding monomer attachment, resulting in a completely random sequence of monomers in the chain. Only one parameter is initially guessed, the probability of a carbon monoxide monomer in the oligomer chain $P(\mathrm{CO})$; the probability of the ethylene monomer is simply the difference between this value and one, $1 - P(\mathrm{CO})$. The theoretical intensities are then calculated by calculating the probability of each possible sequence at a given length and summing these values for all sequences of the same composition. Because the distribution is random, the probability of the carbon monoxide monomer in any chain is the same as the composition of the copolymer.

In the first-order Markovian model, addition of a monomer to an oligomer chain is assumed to be dependent on the preceding monomer, as the reactivity of the monomers is different. In this case, two parameters are initially guessed, P_{COCO} and P_{EE}, the probabilities of adding a carbon monoxide to a chain ending in a carbonyl, and adding an ethylene to a chain ending in an ethylene, respectively. From these values, the probability of an ethylene adding to chain ending in carbonyl, P_{COE}, and the probability of a carbon monoxide

Table 1. Results from Statistical Modeling of Experimental Data

model type	% CO calcd	agreement factor	N_E	N_{CO}
Bernoullian	22 ± 1	0.49 ± 2		
Markovian	21 ± 1	0.24 ± 1	3.6	1.0

adding to a chain ending in carbonyl, P_{ECO}, are calculated, $P_{COE} = 1 - P_{COCO}$ and $P_{ECO} = 1 - P_{EE}$. Using these four values, the probability of particular sequence is calculated. The theoretical intensity of a peak is then determined from the sum of the probabilities of all possible sequences of a particular composition and length.

With both models, modeling was performed using a modification of a procedure described in detail elsewhere.[29] Initial values for parameters in each model are guessed, and the theoretical distribution is calculated from the theoretical intensities of each peak. The theoretical distribution is then compared to the experimental data, and the average agreement factor is determined. The agreement factor for each oligomer series is calculated by the sum of the absolute values of the difference between the normalized experimental peak area and the theoretical peak probability from the model for each peak in an oligomer series. The values are incremented until the minimum average agreement factor between the theoretical and experimental data is found.

Table 1 shows the average molar composition and agreement factor obtained from best-fit modeling using both Bernoullian and first-order Markovian models on the singly saturated ^{107}Ag cationized oligomers of length 12−22. In the case of the Markovian model, the number-average sequence lengths are also listed, calculated from the values of P_{EE} and P_{COCO} obtained from the model: $N_E = (1 - P_{EE})^{-1}$ and $N_{CO} = (1 - P_{COCO})^{-1}$. Composition obtained in both cases, 22 ± 1% in the case of the Bernoullian model and 21 ± 1% for the Markovian, is similar to that obtained by direct calculation from the spectra and comparable but slightly higher than that obtained by NMR (18.2%). The agreement factor is substantially better (lower) for the Markovian model than the Bernoullian, indicating a better agreement of the oligomer sequences to Markovian behavior rather than random association. Although the overall average agreement factor for the Markovian model was 0.24, the average agreement factor for the three spectra at each oligomer length went down as oligomer length increased. This is likely due to the statistically limited number of peaks for modeling in a distribution at smaller oligomer lengths and the larger number of peaks present at higher lengths.

Using the Markovian model, the number-average sequence length of ethylene was found to be 3.6 and of carbon monoxide, 1.0. These values suggest that the reactivity of a carbon monoxide monomer to a chain ending in a carbon monoxide is extremely low, while the reactivity of an ethylene to an ethylene or carbon monoxide terminated chain is significantly higher. From this, it is believed E/CO oligomers examined here have an alternating structure in which almost no carbon monoxide monomers are found sequentially. Instead, lengths of ethylene chain alternate with single carbon monoxide monomers. This structure is in good agreement with the observation that homopolymerization of carbon monoxide is not energetically favorable; i.e., carbon monoxide monomers do not add to a chain terminated in a carbon monoxide.[13] The sequence length of 1.0 for carbon monoxide corresponds to this unfavorable addition of multiple carbon monoxides.

Conclusions

MALDI mass spectra can be obtained for low molecular weight ethylene−carbon monoxide copolymers using proper experimental conditions. Because of similar monomer masses, the oligomers of different composition but the same length occur at the same nominal mass-to-charge ratio, prohibiting low resolution analysis with TOF instrumentation. Chemical reduction was explored but found unsuccessful as a means to increase the mass of the carbon monoxide monomers to differentiate oligomers, likely due to the inability to ionize fully reduced oligomers. High-resolution spectra were obtained using MALDI-FT-ICR wherein the isobaric ECO oligomers could be fully resolved. Compositions determined directly from the spectra and by Bernoullian and first-order Markovian statistical modeling were found to be comparable to those obtained by other methods. From the Markovian model, the oligomers were found to have no sequential carbon monoxide monomers, but instead single carbonyls alternating with random lengths of ethylene.

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