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"Covalent cationization method" for the analysis of polyethylene by mass spectrometry

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Abstract

Polyethylene and other polyolefins have not been amenable to mass spectrometric characterization of molecular mass distribution due to the ineffectiveness of conventional methods of cationization. The lack of polar groups, unsaturation, and aromaticity excludes cationization methods that are used commonly for polymers. A new method is introduced in which an organic cation is covalently bonded to the polymer to produce the necessary ionization for successful matrix-assisted laser desorption/ionization (MALDI) time-of-flight mass spectrometry. A strong MALDI signal results from modified polymers that give no response in their unmodified form.

Keywords: Matrix-assisted laser desorption/ionization; Polyethylene; Polyolefin

1. Introduction

Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS) of synthetic polymers can yield qualitative information about end groups and repeat units, and also quantitative information, such as molecular masses and molecular mass distributions (MMD) [1,2]. However, such measurements can only be made on a select group of polymers. Polyolefins, which include polyethylene (PE), polypropylene, polyisobutylene, poly(methyl pentene), etc. have not been analyzed by MALDI for molecular masses in excess of 2000 g mol^{-1}.

Polyolefins cannot be analyzed by MALDI using existing techniques due to the inefficiency of the cationization process. Cationization by metals such as sodium, potassium, silver, copper, etc. involves association of the cations with functional groups on the polymers. Examples of functional groups include the carbonyl groups of methacrylate polymers, the double bonds of diene polymers, and the phenyl groups of styrenics. Polymers that lack polar, unsaturated, or aromatic groups have not yet been analyzed by MALDI.

Cationization of MALDI samples of synthetic polymers is provided through addition of metal cations to the polymers. The addition can be inadvertent and uncontrolled such as by the extraction of sodium ions from glassware for poly(methyl methacrylate) [3], or by addition of metal salts such as silver or copper to polystyrene [4]. Such procedures can provide MALDI signals, but the total amount and stability of the cationization is poorly understood.

Polyethylene has been cationized by this approach with silver, but only for technical waxes, $M < 2000$ g mol^{-1} [5], saturated crude oil fractions [6], long chain alkanes [7], and for hydrogenated polybutadiene, $M < 2000$ g mol^{-1} [8]. Higher molecular mass characterization was not possible. Polyethylene with 'living' Ziegler–Natta catalyst has been analyzed for $M < 2000$ g mol^{-1} [9], but was specific to the system and not possible for higher molecular masses.

Polyolefins dominate the market share of synthetic polymer production. While it is one of the polymer classes with the longest production history, new developments in metallocene catalysts have caused a great resurgence of activity and have resulted in a wide variety of new applications and increased raw material production [10]. The new catalysts can provide unprecedented control of polymer molecular mass and MMD, co-polymerization control, stereochemistry, etc. MALDI has provided valuable information on the nature of the polymerization process and the resultant structure for many other polymer types, but not for polyolefins. If polyolefins could be routinely analyzed by MALDI, development time for new catalysts and polymers could be greatly reduced.

In this report, we describe a novel method of placing

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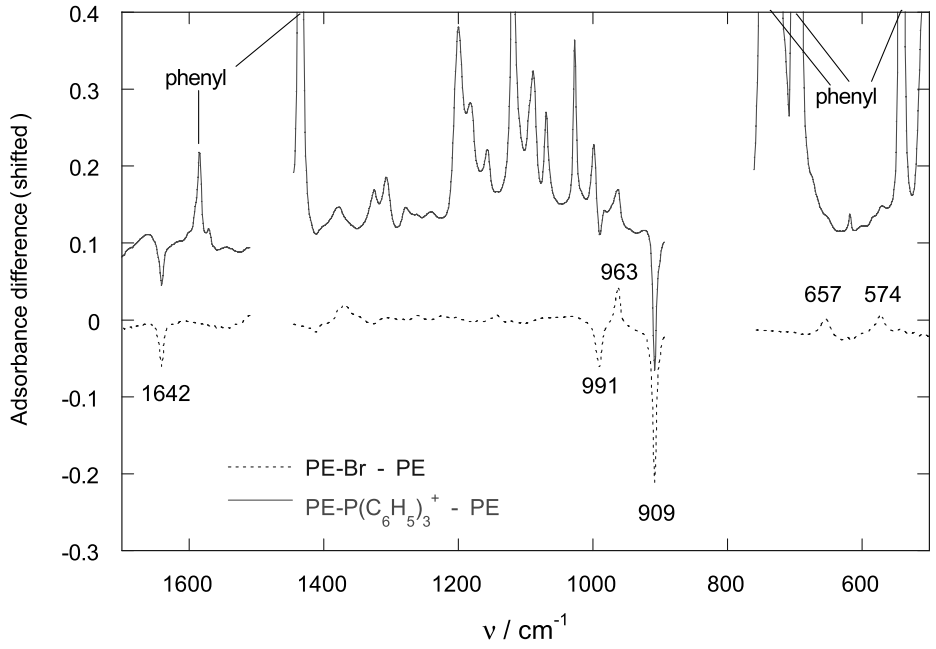

Fig. 1. Difference FTIR spectra of brominated PE − PE (dashed curve) and TPP PE − PE (solid curve). Numbers on plot are values of spectral features in cm^{-1}.

charges that are covalently bonded to the PE. The modified PE produces strong MALDI signals capable of being processed by conventional MALDI data analysis techniques.

2. Experimental

The chemical modification involves two synthetic steps on a PE, NIST standard reference material, SRM 2885. A solution of PE in toluene is prepared by heating the mixture to 110°C. Excess bromine (>10× molar excess) is added and kept at 110°C for 4 h and then the reaction product is precipitated into methanol. The polymer is redissolved in xylene and excess triphenyl phosphine (TPP) (>10× molar excess) is added. It is then precipitated into methanol and dried in vacuum.

Products of the reaction of PE with bromine and TPP were analyzed by Fourier transform infrared spectroscopy. The samples were purified by precipitation into a large excess of methanol to remove any unreacted TPP. The infrared samples were films, approximately 0.015 cm thick, prepared by hot pressing at approximately 130°C. Spectra were recorded at 2 cm^{-1} resolution on a Nicolet Magna System 550 FTIR equipped with a DTGS detector.[1] The co-addition of 100 scans gave adequate signal-to-noise to perform spectral subtraction to enhance spectral features resulting from chemical modification of the samples.

[1] Certain commercial materials and equipments are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Dithranol or all-*trans* retinoic acid were each shown to perform satisfactorily as MALDI matrices. The data presented were taken using all-*trans* retinoic acid. Toluene or xylene were used as the solvents and heated to >100°C to put the analyte into solution. Solution concentrations were typically 40 mg/ml for the matrices and 1 mg/ml for the analyte. The two solutions were mixed in a 1:1 ratio and hand spotted from a glass micropipette onto the steel target. The pipettes were heated to limit cooling of the solution during spotting. The dried droplets showed a finely divided crystalline structure.

MS was performed on a Bruker REFLEX II instrument in reflectron mode using delayed extraction.[1] Ions were generated using a 337 nm wavelength nitrogen laser with a pulse duration of the order of 3 ns and an average energy of approximately 5 μJ spread over a spot size of $200 \times 50\ \mu m^2$. The laser power used was slightly higher than typically used for other polymers (e.g. polystyrene with silver cationization). All data shown are for positive ions: negative ion spectra typically produced only matrix ions and their clusters, e.g. M^-, $2M^-$, etc. The instrument was periodically calibrated with bovine insulin using the $[M + H]^+$ and $[M + 2H]^{+2}$ peaks which provide uncertainties of less than a few mass units.

3. Results and discussion

3.1. FTIR

Fig. 1 shows the difference spectra obtained by subtracting the spectrum of SRM 2885 from the brominated PE, and from the product of addition of TPP to the brominated PE.

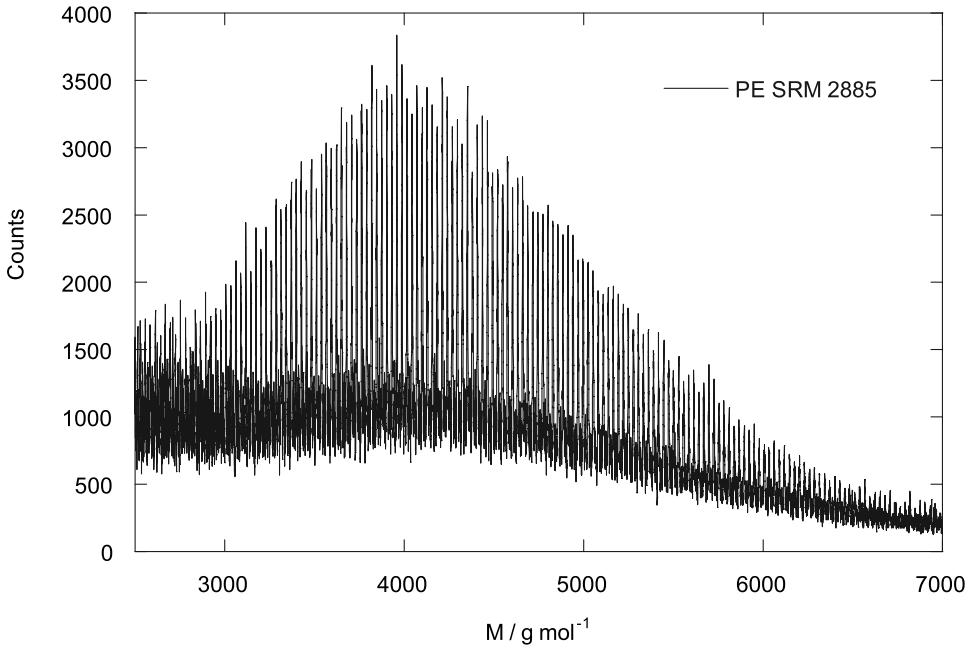

Fig. 2. MALDI–TOF–MS of chemically modified PE, in this case NIST Standard Reference Material 2885.

The normalized absorbance curves are subtracted from each other to emphasize the differences due to the chemical modification. The bottom curve shows the subtraction of the as-polymerized PE from the brominated sample in the frequency range of $\nu = 1700$–$500\ cm^{-1}$ that contains bands characteristic of vinyl groups (909 and 991 cm^{-1}), carbon–carbon double bonds, 1642 cm^{-1}, and bromine–carbon bonds (574 and 657 cm^{-1}). The negative peaks (909, 991 and 1642 cm^{-1}) indicate that vinyl groups have been consumed in the bromination step. Bromination of PE has been used in the analysis of unsaturation [11], including resolution of vinylidene and methyl components of the 888 cm^{-1} band [12]. The appearance of vinyl bands at 909 and 991 cm^{-1}, and the carbon–carbon double bond stretch at 1642 cm^{-1} in the spectrum of the brominated PE indicates that the bromination reaction was incomplete. Although the positive peak at 963 cm^{-1} in the difference spectrum, Fig. 1 (bottom curve), may be due to bromination it was not observed by Rueda et al. [11] in samples brominated by exposure to bromine vapor in the solid state. The 963 cm^{-1} band appeared in the infrared spectra of other PE samples that were brominated by the solution procedure used here.

The top curve shows the subtraction of the as-polymerized PE from the brominated sample that was treated with TPP. The difference peaks at 909 and 991 cm^{-1} are the same intensity as in the previous difference curve showing that the remaining vinyl groups in the brominated PE are unaffected by the addition of the TPP. However, infrared bands appear that are characteristic of aromatic groups. The presence of the aromatic adsorptions in the final sample indicates that there has been a covalent attachment of the phosphonium ions.

The vinyl content of SRM 2885 is determined from the 909 cm^{-1} band based on an integrated absorbance obtained from analysis of the infrared spectrum of 1-octene. The determined value, (0.125 ± 0.01) C=C per 100 C, corresponds to approximately one vinyl group for every two molecules as estimated from the certified mass average molecular mass of SRM 2885, 6280 g mol^{-1}, and polydispersity of 1.13 as characterized by light scattering and gel permeation chromatography [13]. The vinyl content is reduced by bromination to a fraction 0.32 ± 0.03 of its value in SRM 2885. A qualitative assessment of the extent of reaction with TPP is made from the infrared data in the absence of spectral data on a model compound of TPP. The intensity of the carbon–bromine stretch band at 574 cm^{-1} in TPP treated PE decreases to approximately 0.3 ± 0.1 of its value in brominated PE. Since two bromines should be attached to the PE on adjacent carbons, but only one would be removed by the formation of the phosphonium ion, the presence of 574 cm^{-1} band is not an indication of an incomplete reaction. Using integrated intensities from alkyl benzenes [14] the phenyl content in TPP treated PE is estimated to be 0.27 phenyl per 100 C or 2 per vinyl group, approximately. Since each phosphonium group contains three phenyls and the reaction yields one phosphonium group per reacted vinyl the qualitative results are in agreement with the observation that approximately 1/3 of the original vinyls remain unreacted by the treatment employed here. Hence, an estimated 1/3 of the original PE molecules are labeled with TPP by the chemistry employed. Therefore, the covalent attachment of the cation is conveniently accomplished by use of the existing unsaturation in the starting PE that is the result of the synthesis [10]. While there is the potential for both bromines

to be reacted with TPP, there is no MALDI signal seen that is due to double charging. However, many other types of chemistry are possible. For example, hydroxy terminated polystyrene, polybutadiene, and hydrogenated polybutadiene (*fau* polyolefin) have been modified at NIST by converting the –OH to –Br by treatment with PBr_3 and then converting to $-N^+(CH_3)_3$ or $-P^+(C_6H_5)_3$ by treatment with trimethyl amine and TPP, respectively. While simple modification of as-polymerized polyolefins with bromine and TPP represents a model case, the covalent cationization method applies to other chemistries and polymer types as well.

3.2. Mass spectrometry

Fig. 2 plots the MALDI–TOF–MS results from SRM 2885 that has been modified by the covalent cationization method. No smoothing or baseline subtraction was used in the data presented in Fig. 2. A strong MALDI signal was produced from the modified PE while the unmodified and the brominated PE produced none. All samples examined show a strong repeating pattern of 28 g mol^{-1}; however, some samples also had a pronounced repeat of 14 g mol^{-1}. This may be due to fragmentation or may be a consequence of the polymerization chemistry of olefins. The abundance of tightly-spaced peaks with 14 g mol^{-1} spacing below 3000 g mol^{-1} suggests the existence of fragmentation. However, these peaks also exist at the high mass end of the spectrum above 6000 g mol^{-1}. It is known that premature chain termination can produce molecules with an odd number of carbon atoms [9], and thus give spacing at 14 g mol^{-1}. It is possible that both of these two effects may occur in this mass spectrum.

To further understand the mass spectrum, the mass autocorrelation function was applied to the data. For the typical polymer mass spectrum, with its many periodic peaks, this is a natural mathematical operation to use. The mass autocorrelation function has a local maximum for each periodic separation of peaks in the original mass spectrum [15]. It is defined as:

$$G(L) = \sum_i S(m_i)\, S(m_{i+L}) / \sum_i S(m_i)\, S(m_i) \quad (1)$$

where $S(m_i)$ is the signal intensity at m_i, m_i takes integer values of mass and L is the lag which defines the distance in mass over which the correlation ranges. To obtain the correct autocorrelation function, the original signal, which has data points that are periodic in time, was interpolated with periodic points in mass at integer values of mass, e.g. at $1u$, $2u$, $3u$, etc. This resulted in the loss of isotopic resolution in the autocorrelation function, but also enhanced its smoothing effect on the data.

The mass autocorrelation function for the data shown in Fig. 2 with a lag, L, up to 100 g mol^{-1} is shown in Fig. 3. It largely replicates the original mass spectrum while reducing

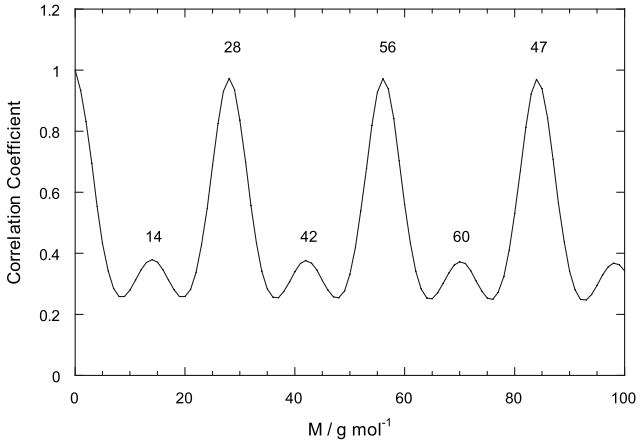

Fig. 3. Mass autocorrelation of the data in Fig. 2. Notice the strong repeat spacing at 28 g mol^{-1} increments and the substantially weaker spacing at 14 g mol^{-1}.

the baseline noise that is expected to be aperiodic. In this way, it can be roughly thought of as a kind of 'averaging'. The peaks at 28 g mol^{-1} are for correlations of a single ethylene repeat unit, those at 56 g mol^{-1} are for two ethylene repeat units, etc. There exists a weaker, but unmistakable, correlation at 14 g mol^{-1} indicating the presence of fragmentation or possible premature chain termination leaving an odd number of carbons in the molecule. The MMD of this polymer is narrow and the intermediate peaks cannot be due to doubly charged polymers of twice the mass. Finally, since the spacing used in this autocorrelation function is 1 g mol^{-1} the isotopic resolution expected at 1 g mol^{-1} increments is not observed, instead autocorrelation within the minor peaks is simply smeared out.

While the MALDI signal is quite strong, it does not necessarily represent the mass distribution of all of the polymer molecules present in the sample. Rather, it only samples the molecules that have been cationically charged. Only PE molecules with double bonds can react with the synthetic method described here. Molecules with double bonds may not have the same MMD as the whole polymer. Also, as is shown by Fig. 1, not all of the double bonds reacted in this example. The M_w of the MALDI characterization is 4500 g mol^{-1} compared to the light scattering value of 6280 g mol^{-1}. If reactivity is dependent on molecular weight, this may also bias the MMD, but from the early work of Flory [16], such effects are usually discounted.

Other methods of chemical modification should eliminate some of these questions. The level of terminal unsaturation is close to 100% in some polyolefins and synthetic techniques with near 100% conversion could be used. Also, random reactions with repeat units along the chain give responses that can be analyzed for MMD. For example, polystyrene has been chloromethylated and then cationically charged with trimethyl amine or TPP producing results that do not have the biasing of vinyl group distributions.

4. Conclusions

The covalent cationization method is an effective way to produce a MALDI response in PE while conventional cationization methods only produce weak signals in low molecular mass samples. It is not presently known if this technique has any biasing in MMD, but work is continuing to address this question to establish if incomplete derivatization, MMD effects, or fragmentation are present.

While the covalent cationization method has potential for polyolefin analysis, it can also be used for the study of other polymers. By covalently attaching charges to polymer chains, a new tool is now available for the investigation of the mechanism of MALDI. Model materials can be made that can probe the ionization mechanisms necessary to the MALDI process.

Acknowledgements

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References

[1] Nielen MWF. Mass Spectrom Rev 1999;18:309–44.
[2] Hanton SD. Chem Rev 2001;101:527–69.
[3] Danis PO, Karr DE. Org Mass Spectrom 1993;28:923–5.
[4] Mowat IA, Donovan RJ. Rapid Commun Mass Spectrom 1995;9:82–90.
[5] Kuhn G, Weidner S, Just U, Hohner G. J Chromatogr 1996;732:111–7.
[6] Dutta TK, Harayama S. Anal Chem 2001;73:864–9.
[7] Chen R, Li L. J Am Soc Mass Spectrom 2001;12:367–75.
[8] Kahr MS, Wilkins CL. J Am Soc Mass Spectrom 1993;4:453–60.
[9] Hinderling C, Chen P. Int J Mass Spectrom 2000;196:377–83.
[10] Peacock AJ. Handbook of polyethylene: structures, properties, and applications. New York: Marcel Dekker, 2000.
[11] Rueda DR, Balta Calleja FJ, Hidalgo A. Spectrochim Acta 1974;30A:1545.
[12] ASTM D 3124-98. Standard test method for vinylidene unsaturation in polyethylene by infrared spectrophotometry. 2000 Annual Book of ASTM Standards, Vol. 08.02, 2000. p. 250–3.
[13] Guttman CM, Maury JR, Blair WR, Schultheisz CR. NISTIR 6454. http://www.nist.gov/msel/div854/maldi/SRM_Certificates.htm 2001.
[14] Wexler AS. Spectrochim Acta 1965;21:1725–42.
[15] Wallace WE, Guttman CM, Antonucci JM. J Am Soc Mass Spectrom 1999;10:224–30.
[16] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press, 1953.