

Application of Nonpolar Matrices for the Analysis of Low Molecular Weight Nonpolar Synthetic Polymers by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

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The application of nonpolar matrices for the analysis of low molecular weight nonpolar synthetic polymers using matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) is demonstrated. Anthracene, pyrene, and acenaphthene were utilized as nonpolar matrices for the analysis of polybutadiene, polyisoprene, and polystyrene samples of various average molecular weights ranging from about 700 to 5000. The standard MALDI-MS approach for the analysis of these types of polymers involves the use of conventional acidic matrices, such as *all-trans*-retinoic acid, with an additional cationization reagent. The nonpolar matrices used in this study are shown to be as equally effective as the conventional matrices. The uniform mixing of the nonpolar matrices and the nonpolar analytes enhances the MALDI-MS spectral reproducibility. Silver salts were found to be the best cationization reagents for all of the cases studied. Copper salts worked well for polystyrene, poorly for polyisoprene, and not at all for polybutadiene samples. These matrices should be useful for the characterization of hydrocarbon polymers and other analytes, such as modified polymers, which may potentially be sensitive to acidic matrices. (J Am Soc Mass Spectrom 2000, 11, 731-737) © 2000 American Society for Mass Spectrometry

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) is becoming a popular analytical technique for the analysis of synthetic polymers. MALDI-MS yields information such as average molecular weight, molecular weight distribution, and repeat-unit and end-group masses. However, various limitations include the applicability of the technique to polymers of narrow polydispersity, lack of common solvents for particular analyte and matrix combinations, and lack of suitable matrices for specific analytes [1, 2].

Although an a priori determination of whether a particular chemical compound will function as a suitable MALDI matrix is not yet possible, several important matrix properties have been identified. These properties include absorption of the matrix compound at the wavelength of the laser used, vacuum stability, solvent compatibility, and adequate isolation of the analyte by

the matrix [3]. A survey of the common matrices which are shown to be suitable for the analysis of nonpolar synthetic polymers finds that each of these matrices is soluble (to some extent) in a suitable organic solvent, although the extent of isolation of the analyte by the matrix is matrix dependent. For example, a study of nonpolar synthetic polymers, mainly polystyrene and polybutadiene, with DHB as a matrix showed that these polymers do not mix well with this matrix [4, 5]. Under microscopic observation, polystyrene crystals were found to be separated from the DHB matrix crystals after mixing and drying [4]. It should be noted, however, that Pastor et al. have found that DHB was superior to IAA and HABA for MALDI Fourier transform ion cyclotron resonance mass spectrometric analysis of nonpolar polymers such as polystyrene and polybutadiene [6].

In general, MALDI-MS has been more successful for the analysis of polar synthetic polymers than for nonpolar synthetic polymers. Polar synthetic polymers have a higher chemical resemblance to biopolymers, such as proteins and peptides, for which the MALDI

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technique was originally developed, and contain heteroatoms such as N or O which provide sites for proton or metal cation attachment [1, 2, 7]. For synthetic polymers, formation of ions via cation attachment is much more favored than via protonation [4, 5]. Water-soluble polymers, such as polyethylene glycol and polypropylene glycol, have been successfully analyzed with MALDI using DHB as a matrix with alkali-metal salt solutions to increase the yield of the cationized species [4]. Other water-soluble polymers, like polyacrylic acid and polystyrene sulfonic acid, have been analyzed using sinapinic acid as a matrix [8]. The organic soluble polar polymers, such as polymethylmethacrylate, polyvinylacetate, and polyvinylchloride, have been analyzed using various matrices including DHB, *t*-3-indoleacrylic acid (IAA) [1, 9] and 2-(4-hydroxyphenylazo)benzoic acid (HABA) [9].

Finding a suitable matrix which will work well for nonpolar polymers has traditionally been through trial and error. The most common MALDI matrices which have been applied to polystyrene include dithranol [10-12], DHB [6], IAA [1, 2, 13], *all-trans*-retinoic acid [14-17], HABA [5], and 2-nitrophenyl octyl ether [4]. These matrices have been used together with cationization reagents such as Ag^+ [2, 14-18], Cu^{2+} , Li^+ , or Na^+ [10].

The presence of the phenyl functionality on polystyrene is considered to be responsible for its higher ionization probability compared to other nonpolar polymers such as polybutadiene, polyisoprene, polyethylene, or polypropylene. To date, there have been no reports in the literature regarding the successful MALDI analysis of polyethylene or polypropylene. The presence of the phenyl group of styrene or the unsaturated double bond on butadiene provides a site of high metal affinity [19]. Such a site is not available on polyolefins, which probably accounts for them being the hardest to analyze by MALDI [15, 20]. However, polyethylene samples have been analyzed using laser desorption Fourier transform mass spectrometry (LD/FTMS) [21].

There are fewer reports in the literature regarding the analysis of polybutadiene and polyisoprene with MALDI-MS than for polystyrene. Polybutadiene and polyisoprene have been analyzed by MALDI using the same or similar matrices as those which have been used for polystyrene. Examples of matrices which have been applied to analyze polybutadiene are azo compounds [5], IAA [2, 13], 1,4-di-[2-(5-phenyl oxazolyl)]benzene [13], 2-nitrophenyl octyl ether [2], *all-trans*-retinoic acid [7], and DHB [6]. Matrices which have been applied to polyisoprene include IAA [2, 13], DHB [6], *all-trans*-retinoic acid [7], and dithranol [12].

Previously, we have found that nonpolar matrices, such as anthracene and terthiophene, are suitable for MALDI-MS analysis of low molecular weight nonpolar analytes [22, 23]. Nonpolar analytes and the nonpolar matrices are soluble in a common organic solvent, which facilitates analyte:matrix cocrystallization upon

spotting on the MALDI sample plate. These nonpolar matrices have low ionization energies and high molar extinction coefficients in the UV, facilitating the production of radical molecular cations of the matrix during the MALDI event.

In our prior work with these matrices, we demonstrated that the use of such matrices results in the production of radical molecular cations of the analytes [22, 23]. A further investigation regarding the ionization mechanism for these matrices found that, in the majority of cases, production of radical molecular cations of the analyte depends upon the difference in ionization energies of the matrix and analyte [23]. When the ionization energy of the matrix is greater than that of the analyte, charge transfer between the matrix radical molecular cation and neutral analyte is thermodynamically favored.

The suitable MALDI-MS properties of these nonpolar matrices led us to consider their applicability for the characterization of nonpolar synthetic polymers. Tang et al. had previously reported that polycyclic aromatic hydrocarbons, such as anthracene, benzo[a]pyrene, chrysene, naphthalene, phenanthrene, and pyrene, did not function as suitable matrices for the analysis of synthetic polymers [24]. However, that study focused primarily on polar synthetic polymers, with the exception of a polybutadiene sample. In this paper, we report the use of nonpolar matrices, such as anthracene, pyrene, and acenaphthene, for the characterization of several low molecular weight nonpolar polymers. In this work, the polymers analyzed included: polybutadiene 760, 1100, and 2940, polystyrene 1940, 2557, 2800, and 5120, and polyisoprene 2300 and 2600 (the numbers represent the mass-weighted average molecular weight of the polymer). We have found that nonpolar matrices are effective for the analysis of nonpolar polymers when a silver salt is included as a cationization reagent. A comparison of the mass spectral data obtained using nonpolar matrices relative to mass spectral data obtained from conventional acidic matrices will be addressed.

Experimental

Chemicals

Anthracene, pyrene, acenaphthene, terthiophene, *all-trans*-retinoic acid, indoleacrylic acid (IAA), copper(II) nitrate, and silver trifluoroacetate (AgTFA) were purchased from Aldrich Chemical (Milwaukee, WI) and used without further purification. Poly(butadiene) 760, 1100, and 2940 were obtained in-house at Dow. The polyisoprene sample, estimated to be polyisoprene 3062, was a gift from Professor Cindy Schauer at the University of North Carolina at Chapel Hill. Polystyrene 1940, 2557, 2800, and 5120 were purchased from Scientific Polymer Products (Ontario, NY). All polymer samples were used as received. HPLC-grade tetrahy-

drofuran (THF) was obtained from EM Science (Gibbstown, NJ) and used as received.

Sample Preparation

All matrices and analytes investigated were dissolved in THF. Saturated solutions of the matrices were used. The concentrations of the polymer solutions ranged between 2×10^{-4} and 5×10^{-4} M. For all analyses, typically 2 μ L of the analyte solution was added to a 10 μ L solution of the matrix and mixed thoroughly. About 1 to 2 μ L of the resulting mixture was spotted onto the sample plate and allowed to air dry at room temperature. For the experiments with cationization reagents [either AgTFA or Cu(NO₃)₂], 2 μ L of a 0.1 M solution of the required reagent in THF was added to a mixture containing 10 μ L of matrix and 2 μ L of analyte. As before, 1 μ L of the resulting mixture was spotted onto the sample plate and allowed to air dry at room temperature.

Mass Spectrometry

All experiments were performed using either a PerSeptive Biosystems (Framingham, MA) Voyager linear time-of-flight mass spectrometer or a Bruker ProFlex (Billerica, MA) time-of-flight mass spectrometer operated in reflectron mode. Both instruments are equipped with a nitrogen laser ($\lambda = 337$ nm). External calibration was performed using anthracene (m/z 178) and C₆₀ (m/z 720). Data were collected with the laser power set just above the ionization threshold of the matrix to avoid fragmentation and to maximize resolution. The standard deviations for the measured M_n and M_w values were determined from the average of three sample loadings. Typically 10–150 scans were averaged to obtain each mass spectrum, with the number of scans being held relatively constant between sample loadings for a particular analyte.

Results and Discussion

General Characteristics of Nonpolar Matrices

In this study, anthracene, pyrene, and acenaphthene were investigated as to their effectiveness as matrices for the analysis of low molecular weight nonpolar synthetic polymers. One of the motivations for examining nonpolar matrices was to improve the interaction between the polymer and matrix by dissolving each in a common solvent. The polymer samples and nonpolar matrices were dissolved in the same solvent (THF) to promote the interaction of the analyte and matrix on the MALDI sample plate [1]. With the use of nonpolar matrices, spectra reproducibility from spot to spot was found to be high. It was also observed that finding a spot which gives a high quality mass spectrum was not difficult. Although there are other factors which influence phase separation between the analyte and matrix

(e.g., the number of chain elements and the Flory–Huggins interaction parameters), these results imply that the sample and matrix interact well and uniformly and that uniform interaction is retained upon solvent evaporation. The polybutadiene, polyisoprene, and polystyrene samples characterized in this paper did not generate representative molecular ions when analyzed as neat samples under the experimental conditions used for the MALDI investigation.

Nonpolar Matrices Without Cationization Reagents

Our initial investigations focused on the suitability of the nonpolar matrices at generating representative mass spectra from nonpolar polymers via charge-transfer ionization. No discernible mass spectral data could be obtained from any of the polymers investigated in this study when pristine sample plates, which had not been previously exposed to silver salts, were used. However, it was found that residual silver salts remaining on previous, cleaned MALDI sample plates were serving to facilitate the cationization of the nonpolar polymers. The vertical ionization energies of the nonpolar matrices and monomers have been determined and evaluated previously [25]: pyrene (IE 7.426 eV), anthracene (IE 7.439 eV), acenaphthene (IE 7.75 eV), styrene (IE 8.464 eV), isoprene (IE 8.86 eV), and butadiene (IE 9.072 eV). Thus, in the case of the analytes investigated in this study, the ionization energies of the matrices lie below those of the monomer units for the various polymers, and charge-transfer ionization would be thermodynamically unfavorable. If matrices with ionization energies greater than the ionization energies of the monomers are available, it would be interesting to examine whether charge-transfer ionization could provide an alternative means of generating mass spectra from nonpolar polymers.

Nonpolar Matrices With Cationization Reagents

After determining that nonpolar matrices are not suitable for the analysis of nonpolar polymers in the absence of cationization reagents, experiments were then performed to examine the suitability of such matrices in the presence of a cationization agent. Table 1 summarizes the results obtained using either nonpolar or traditional MALDI matrices. Among several traditional (polar) matrices, *all-trans*-retinoic acid was used as a representative matrix for this work. Each entry presented in Table 1 is an average of three experimental results. Discussion of these results is presented below.

Polystyrene

Figure 1 contains representative mass spectral data of polystyrene 1940 which was analyzed using anthracene

Table 1. Comparison of MALDI-MS and GPC data for hydrocarbon polymers. All masses were corrected for Ag or Cu, respectively. Data were acquired using a reflectron TOF except where noted. Standard deviations were determined from three separate sample loadings. The approximate number of scans averaged per sample loading is given in parentheses

Polymer	M_w	M_n	M_w/M_n	Method
Polystyrene 1940	2052 ± 43	1960 ± 33	1.05	anthracene/Ag (20 scans/sample)
	2499 ± 54	2413 ± 42	1.04	anthracene/Cu (16 scans/sample)
	2287 ± 33	2197 ± 28	1.04	pyrene/Ag (25 scans/sample)
	1998 ± 71	1867 ± 50	1.06	RTA/Ag ^a (16 scans/sample)
	2148 ± 71	2031 ± 70	1.06	RTA/Cu ^a (16 scans/sample)
Polystyrene 2557	1940	1690	1.15	GPC
	2592 ± 60	2497 ± 57	1.04	anthracene/Ag ^a (16 scans/sample)
Polystyrene 2800	2557	2500	1.02	GPC
	2852 ± 23	2778 ± 28	1.03	anthracene/Ag (60 scans/sample)
	2996 ± 16	2918 ± 16	1.03	anthracene/Cu (170 scans/sample)
	2697 ± 87	2584 ± 107	1.04	RTA/Ag ^a (12 scans/sample)
Polystyrene 5120	2871 ± 12	2766 ± 31	1.04	RTA/Cu ^a (14 scans/sample)
	—	—	—	GPC (no values given)
	5484 ± 6	5369 ± 8	1.02	anthracene/Ag ^a (13 scans/sample)
	5246 ± 68	5114 ± 156	1.03	RTA/Cu ^a (14 scans/sample)
	5120	4760	1.08	GPC
Polybutadiene 760	795 ± 38	736 ± 36	1.08	anthracene/Ag ^a (14 scans/sample)
	—	—	—	GPC (no values given)
Polybutadiene 1100	1190 ± 70	1101 ± 92	1.08	anthracene/Ag ^a (15 scans/sample)
	1244 ± 13	1179 ± 14	1.06	RTA/Ag ^a (16 scans/sample)
	1300 ± 19	1234 ± 26	1.05	RTA/Cu ^a (16 scans/sample)
	1100	1050	1.05	GPC
Polybutadiene 2940	2960 ± 10	2901 ± 17	1.02	anthracene/Ag (54 scans/sample)
	3030 ± 17	2981 ± 16	1.02	RTA/Cu (60 scans/sample)
	—	—	—	GPC (no values given)
Polyisoprene 3062	2523 ± 26	2408 ± 33	1.04	anthracene/Ag (113 scans/sample)
	2613 ± 113	2511 ± 130	1.04	anthracene/Cu (154 scans/sample)
	2622 ± 57	2498 ± 60	1.05	RTA/Ag ^a (16 scans/sample)
	2620 ± 42	2495 ± 32	1.05	RTA/Cu ^a (16 scans/sample)
	3062	3353	1.09	GPC

^aSpectra obtained in linear mode.

(Figure 1a) and *all-trans*-retinoic acid (Figure 1b) as matrices. In both cases, silver trifluoroacetate (AgTFA) was added as the cationization reagent. The oligomer distributions are similar between the two matrices investigated. In general, it was found that, under similar experimental conditions, anthracene yielded a cleaner mass spectrum, as measured by the baseline signal, than *all-trans*-retinoic acid especially when Ag was used as a cationization reagent. As shown in Figure 1b, the use of *all-trans*-retinoic acid generally resulted in a higher background level with several interfering ions at low m/z values. We observed that when Ag salts are used with *all-trans*-retinoic acid (or other acidic matrices) for MALDI-MS analysis an interfering background signal due to silver clusters may be present up to around m/z 7000.

Similar results were obtained for the analysis of polystyrene 2557, 2800, and 5120. In general, anthracene yielded more abundant and reproducible results than did pyrene or acenaphthene. Acenaphthene has the lowest enthalpy of sublimation of the three matrices which limited the time frame available for obtaining mass spectral data from these samples. Nonpolar matrices with silver cationization reagents tend to yield lower molecular weight distributions for polystyrene

than do nonpolar matrices with copper cationization reagents. In addition, the molecular weight distributions determined using nonpolar matrices are consistently higher than those determined using *all-trans*-retinoic acid as a matrix. However, as discussed further below, these trends do not apply for the analysis of the polydienes. In general, fairly good agreement was found between the MALDI-MS and GPC determined values, with the MALDI-MS results yielding higher number- and weight-average molecular weights as compared to the GPC results.

Polybutadiene

The MALDI results obtained from polybutadiene 2940 using anthracene and *all-trans*-retinoic acid as matrices is shown in Figure 2a, b. In Figure 2a, AgTFA was included as a cationization reagent, and in Figure 2b, Cu(NO₃)₂ was included as a cationization reagent. In general, similar results were found using these different matrix preparations. However, a couple of differences are noted when comparing the mass spectral results obtained with the nonpolar matrices versus those obtained with *all-trans*-retinoic acid. Unlike the situation for polystyrene, the nonpolar matrices consistently

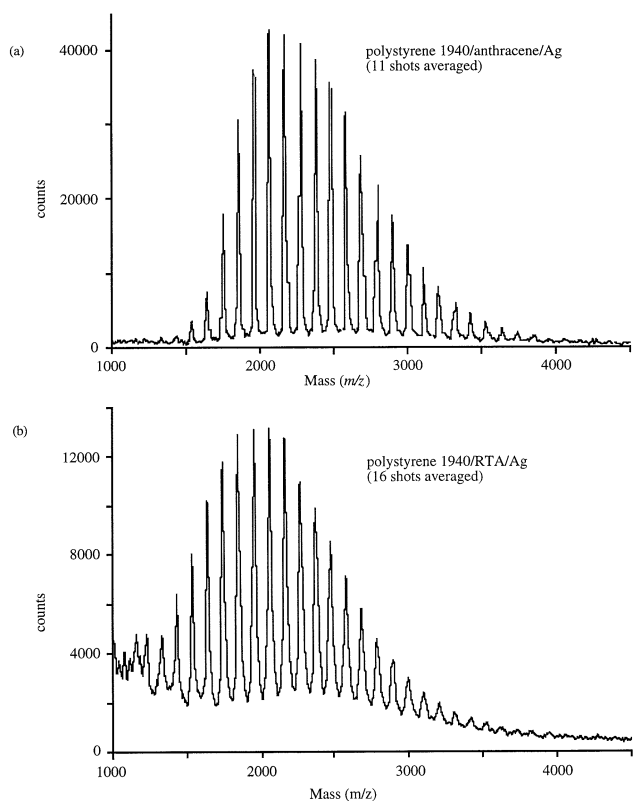


Figure 1. Linear-mode MALDI-TOF mass spectra of polystyrene 1940 with (a) anthracene and (b) *all-trans*-retinoic acid as the matrices. AgTFA was used as the cationization reagent in both cases.

yielded molecular weight distributions that were lower than those obtained using *all-trans*-retinoic acid. Furthermore, where comparisons could be made, the molecular weight distributions obtained using nonpolar matrices were in better agreement with the GPC-determined distributions than those obtained using the polar matrix.

No discernible mass spectral data for polybutadiene could be acquired when $\text{Cu}(\text{NO}_3)_2$ was used as a cationization reagent with any of the nonpolar matrices under experimental conditions used in this work. Higher quality mass spectral data were repeatedly obtained using anthracene as the matrix as compared to pyrene or acenaphthene, although all three matrices were effective for the analysis of the polybutadiene samples.

Polyisoprene

Figure 3 contains representative mass spectra arising from the analysis of a polyisoprene sample with anthracene as the nonpolar matrix in the presence of AgTFA (Figure 3a) and $\text{Cu}(\text{NO}_3)_2$ (Figure 3b) as cationization reagents and *all-trans*-retinoic acid with $\text{Cu}(\text{NO}_3)_2$ (Figure 3c). Similar to the results found for polybutadiene, $\text{Cu}(\text{NO}_3)_2$ is a poorer cationization reagent for polyisoprene analysis with the nonpolar matrices than is

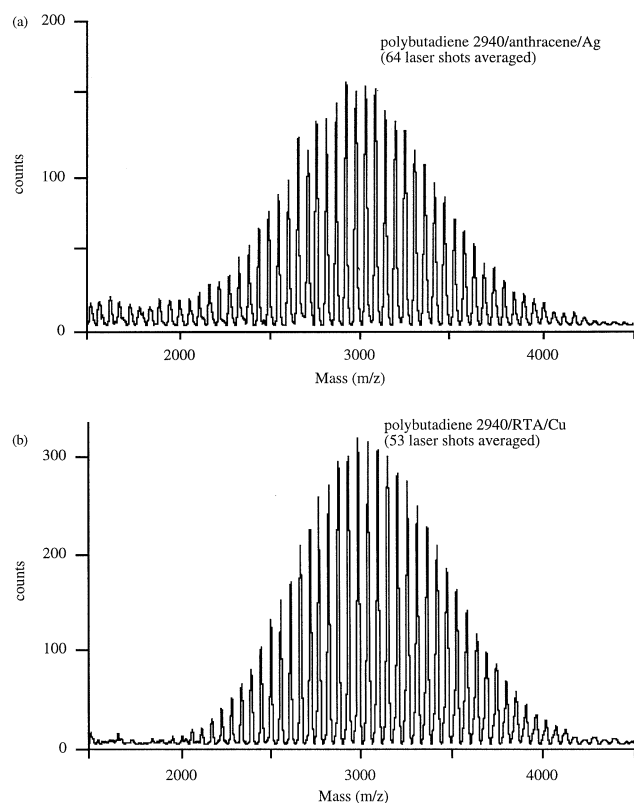


Figure 2. Reflectron-mode MALDI-TOF mass spectra of polybutadiene 2940 with (a) anthracene as the matrix and AgTFA as the cationization reagent and (b) *all-trans*-retinoic acid as the matrix and $\text{Cu}(\text{NO}_3)_2$ as the cationization reagent.

AgTFA. In Figure 3a, a well-defined polymer distribution can be detected when AgTFA is used as the cationization reagent. However, as seen in Figure 3b, the quality of the mass spectral results decreases dramatically when $\text{Cu}(\text{NO}_3)_2$ is incorporated as the cationization reagent. The calculated mass and number weighted distributions for the polyisoprene sample presented in Table 1 show that analysis of this sample using anthracene with Cu exhibits the lowest reproducibility as well as an overall low ion yield (as demonstrated in Figure 3b).

Ag vs. Cu Cationization Reagents

At this time it is not clear why $\text{Cu}(\text{NO}_3)_2$ is not a suitable cationization reagent for the analysis of polybutadienes with nonpolar matrices such as anthracene. Ehring et al. have shown that many matrices upon laser irradiation produce free radicals and electrons which are capable of reducing Cu^{2+} to Cu^+ [26]. Fisher et al. has shown that the most intensive positive ion produced by laser ablation of CuS is Cu^+ [27], and many Cu^+ -alkene complexes are known [28]. In addition, Yalcin et al. have previously found that $\text{Cu}(\text{NO}_3)_2$ is the preferred cationization reagent (vs. Ag salts) for the analysis of high molecular weight polybutadienes [7]. Possible explanations for the results obtained in this

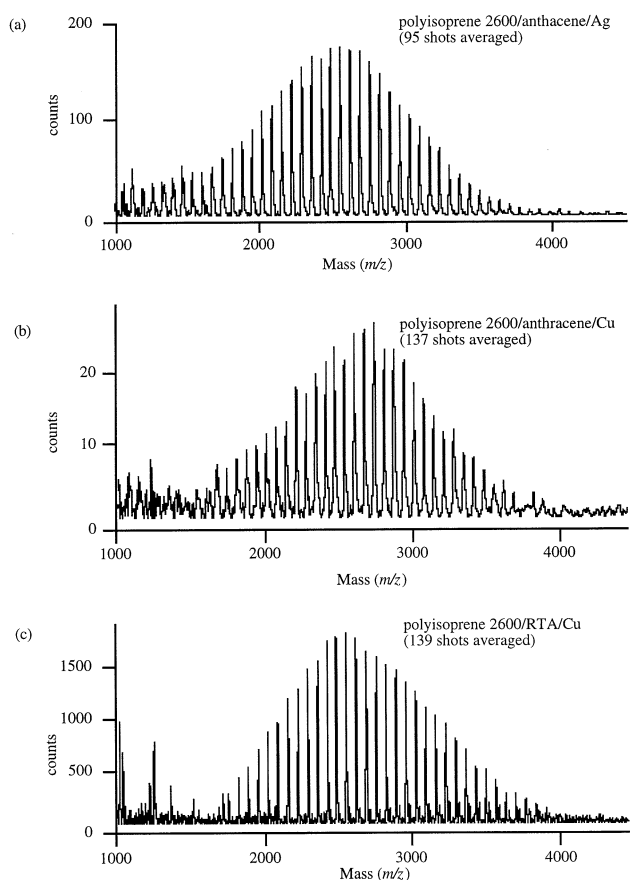


Figure 3. Reflectron-mode MALDI-TOF mass spectra of polyisoprene with (a) anthracene as the matrix and AgTFA as the cationization reagent, (b) anthracene as the matrix and $\text{Cu}(\text{NO}_3)_2$ as the cationization reagent, and (c) *all-trans*-retinoic acid as the matrix and $\text{Cu}(\text{NO}_3)_2$ as the cationization reagent.

work could include a higher interaction between the nonpolar matrix and Cu (as compared to polar matrices and Cu), poor mixing of the cationization reagent with the analyte/matrix solution upon crystallization [19], Cu salts are more reactive in acidic media, or the photoelectrons produced during the ionization event reduce Cu^{2+} to Cu^0 .

Lehmann et al. previously discussed the role of preformed ions in the analysis of polystyrene performed in the presence of a cationization reagent [19]. In that work, the authors suggested that the use of nonpolar matrices favors a situation where the transition metal cation and its counterion crystallize separately from the polystyrene sample, which cocrystallizes with the matrix. Under those experimental conditions, no preformed ions of polystyrene and the transition metal cation are expected to be present; only gas-phase reactions can lead to the production of polystyrene–cation adducts. Although both AgTFA and $\text{Cu}(\text{NO}_3)_2$ each yielded similar, high-quality results for the analysis of polystyrene samples with nonpolar matrices, a similar situation does not exist for the polybutadiene or polyisoprene samples.

The results obtained by MALDI-TOFMS in this study

using nonpolar matrices with Ag are comparable to those obtained previously by other groups [6, 7, 13]. In general, we have found that the use of nonpolar matrices, such as anthracene, yield reproducible results for the analysis of lower molecular weight nonpolar polymers. Although the absolute values for the mass and number average molecular weights obtained using MALDI-MS are not in exact agreement with those values obtained using GPC, the variability in the values obtained using nonpolar matrices is similar to, or better than, the variability found when RTA is used as the matrix.

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