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Role of a UV Absorber as a Matrix for Analysis of Polystyrene Using Matrix-Assisted Laser Desorption/Ionization-Mass Spectrometry

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Matrix-assisted laser desorption/ionization (MALDI) has been widely used as a soft ionization technique and matrix-assisted laser desorption/ionization-mass spectrometry (MALDI-MS) has been used to characterize polymeric materials.[1-5] MALDI is achieved in two steps.[6-9] In the first step, a mixture solution of an analyte and a matrix is spotted on the sample plate, and is dried before analysis. A solid solution deposit of analyte-doped matrix crystals is obtained, and the analyte molecules are completely isolated from each other by embedding throughout the matrix. The second step involves ablation of the solid solution by pulse laser. The pulse laser irradiation induces rapid heating to cause sublimation of the matrix crystals and ionization can occur during this process. Selection of the matrix in MALDI-MS absolutely affect the MALDI process.[1,2]

o-Hydroxyphenyl benzotriazole and hydroxyphenyl triazine derivatives are commonly used as UV absorbers. They absorb destructive UV radiation and dissipate the energy in the form of heat.[9-15] In general, the UV absorbers absorb UV wavelength between 295 and 400 nm, so they can potentially play a role as a matrix in MALDI analysis.[16,17] In this study, the UV absorbers were employed as the matrix to analyze polystyrene (PS) using MALDI-MS. The UV absorbers absorb UV radiation well, are not expensive, and are easily available materials. The analytical results using the UV absorbers were compared with that using anthracene-1,8,9-triol (DIT). DIT is the most common matrix for MALDI-MS analysis of PS.[1,18,19]

Tinuvin 234, Tinuvin 326, Tinuvin 327, Tinuvin 328, Tinuvin 329, Tinuvin 360, and Tinuvin P are UV absorbers of *o*-hydroxyphenyl benzotriazole derivatives. Tinuvin 1577 is a UV absorber of a hydroxyphenyl triazine derivative. Figure 1 shows the MALDI-MS spectra of PS obtained from the samples prepared using DIT and Tinuvin 234 as the matrix. Abundances of the $[PS + Ag]^+$ ions of the MALDI mass spectrum obtained using Tinuvin 234 were larger than those obtained using DIT by about twice. It is a very interesting result because DIT is known to be a proper matrix for MALDI-MS analysis of PS. The average molecular weights were about 4,000-4,200 as listed in Table 1. The average molecular weights for the Tinuvin 234 case were slightly larger than those for the DIT one by about 4%. The other UV absorbers of Tinuvin 326, Tinuvin 327, Tinuvin 328, Tinuvin 329, Tinuvin 360, Tinuvin P, and Tinuvin 1577 were also employed as the matrix, and the analysis results are

Table 1. Average molecular weights of the PS obtained from the MALDI-MS analysis using anthracene-1,8,9-triol and Tinuvin 234. The M_n and M_w denote the number and weight average molecular weights, respectively

Matrix	M_n	M_w
Anthracene-1,8,9-triol	$3.99 \times 10^3 \pm 78$	$4.08 \times 10^3 \pm 76$
Tinuvin 234	$4.18 \times 10^3 \pm 16$	$4.22 \times 10^3 \pm 15$

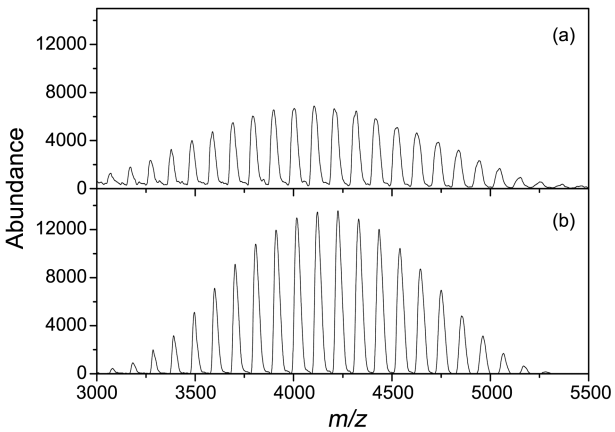


Figure 1. MALDI-MS spectra of PS obtained using anthracene-1,8,9-triol (a) and Tinuvin 234 (b) as the matrix.

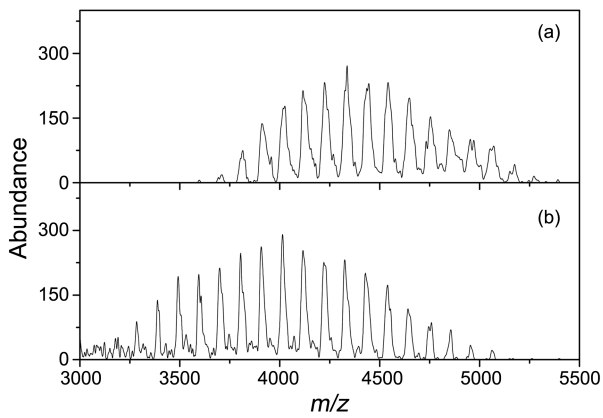


Figure 2. MALDI-MS spectra of PS obtained using Tinuvin 328 (a) and Tinuvin 329 (b) as the matrix.

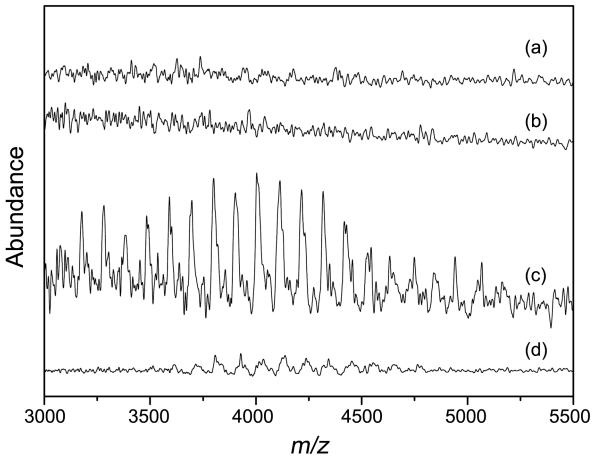


Figure 3. MALDI-MS spectra of PS obtained using Tinuvin 326 (a), Tinuvin 327 (b), Tinuvin P (c), and Tinuvin 1577 (d) as the matrix.

shown in Figures 2 and 3.

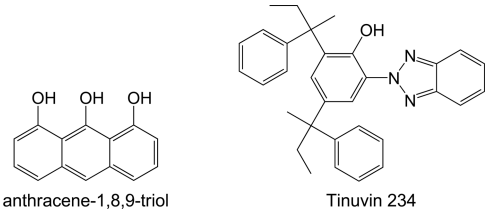
For the Tinuvin 328 and Tinuvin 329 cases, the MALDI-MS spectra displayed some $[PS + Ag]^+$ ions but their intensities were much lower than the DIT and Tinuvin 234 cases. And the ion distributions of the Tinuvin 328 and Tinuvin 329 cases were different from those of the DIT and Tinuvin 234 ones, especially the Tinuvin 328 one as shown in Figure 2. For the Tinuvin 326, Tinuvin 327, and Tinuvin 1577 cases, the MALDI-MS spectra did not display ion distributions of the $[PS + Ag]^+$ as shown in Figure 3. The MALDI-MS spectrum obtained using Tinuvin P showed ion distribution of the $[PS + Ag]^+$, but the baseline was not stable and the sensitivity was very low. For the MALDI-MS analysis using Tinuvin 360 as the matrix, any traces of the $[PS + Ag]^+$ ions were not observed.

The order of the ionization efficiencies according to the matrix was Tinuvin 234 > DIT >> Tinuvin 329 > Tinuvin 328 > Tinuvin P > Tinuvin 1577 > Tinuvin 326, Tinuvin 327 > Tinuvin 360. This can be explained by the compatibility of PS with the matrix because all the matrices may absorb the UV laser (N_2 laser) light of 337 nm well. Since PS has lots of phenyl rings, the matrix having many phenyl rings may be favorable to be compatible with PS. Tinuvin 234 has four phenyl rings. Although Tinuvin 360 also has four phenyl rings, there was no signal of the $[PS + Ag]^+$ ions in the mass spectrum. Tinuvin 360 has two bulky C8 alkyl groups as well as four phenyl rings as shown in Scheme 3. The bulky alkyl groups may prevent compatibility between PS and the matrix. Hence, it can say that a matrix having bulky alkyl groups is not favorable to enhance the ionization efficiency of PS in MALDI-MS analysis. Though Tinuvin 234 has two C4 alkyl groups, the alkyl groups are located between phenyl rings and may be not exposed by the steric hindrance. Both of Tinuvin 328 and Tinuvin 329 have two phenyl rings, while their alkyl groups are different from each other. They have two C5 alkyl groups and one C8 alkyl group, respectively. Ion distribution of the $[PS + Ag]^+$ in the MALDI-MS spectrum obtained using Tinuvin 328 shifted to the higher mass compared to those obtained using DIT and Tinuvin 234 as shown in Figures 1 and 2. Tinuvin 326, Tinuvin 327, and Tinuvin P have two phenyl rings. However, the kinds and numbers of their alkyl groups are different from each other. Tinuvin 326 has one methyl and one C4 alkyl groups, Tinuvin 327 has two C4 alkyl groups, and Tinuvin P has only one methyl group. Of the MALDI mass spectra obtained using Tinuvin 326, Tinuvin 327, and Tinuvin P, the mass spectrum obtained using Tinuvin P showed a relatively better spectrum as shown in Figure 3. Though Tinuvin 1577 has three phenyl rings and only one alkyl group, its MALDI mass spectrum was not good. This may be because its alkyl group is hexyl which is relatively long and is exposed out.

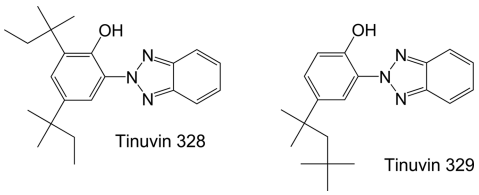
The MALDI-MS spectrum of PS obtained using Tinuvin 234 as the matrix showed an excellent ion distribution of the $[PS + Ag]^+$ and its ionization efficiency exceeded over that obtained using the common matrix of DIT. In addition, the price of Tinuvin 234 is cheaper than that of DIT by about ten times. Therefore, Tinuvin 234 is a recommendable matrix for MALDI-MS analysis of PS due to the high ionization efficiency and high cost-effectiveness.

Experimental Section

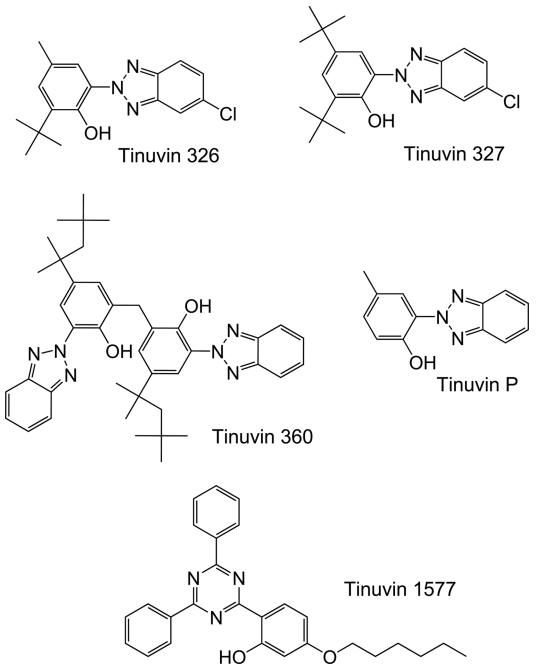
Polystyrene (PS, M_w = 3700) was purchased from Sigma Aldrich Co. Anthracene-1,8,9-triol (DIT), 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (Tinuvin 234), 2-*tert*-butyl-6-(5-chloro-benzotriazol-2-yl)-4-methylphenol (Tinuvin 326), 2-(2-hydroxy-3,5-di-*tert*-butylphenyl)-5-chloro benzotriazole (Tinuvin 327), 2-(2*H*-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (Tinuvin 328), 2-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (Tinuvin 329), 2-2-methylenebis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (Tinuvin 360), 2-(2*H*-benzotriazole-2-yl)-4-methylphenol (Tinuvin P), and 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)-phenol (Tinuvin 1577) were also purchased from Sigma Aldrich Co. DIT and the UV absorbers were employed as the matrix for PS analysis. Chemical structures of the matrices are shown in



Scheme 1. Chemical structures of anthracene-1,8,9-triol and Tinuvin 234.



Scheme 2. Chemical structures of Tinuvin 328 and Tinuvin 329.



Scheme 3. Chemical structures of Tinuvin 326, Tinuvin 327, Tinuvin 360, Tinuvin P, and Tinuvin 1577.

Schemes 1-3. Tetrahydrofuran (THF) and silver trifluoroacetate (AgTFA) were also purchased from Sigma Aldrich Co. AgTFA was used as the cationizing agent.

Each PS, matrix, and AgTFA was dissolved in THF to make 10 mM solution. The average molecular weight (M_w = 3700) of the PS was employed as its molecular weight. The PS, matrix, and AgTFA solutions were mixed by the volume ratios of 1:10:1, and 1.0 μL of the mixing solution was spotted on the sample plate and dried in the air.

MALDI mass spectra were obtained with Axima-LNR MALDI-TOFMS (Kratos-Shimadzu Co. of Japan). Ions were produced by irradiation of the sample with a nitrogen laser (337 nm). Profiling of the product ions was achieved in the positive mode using a linear TOF. The accelerating voltage was 20 kV. The sum of 100 shots was collected for each spectrum.

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