Analysis of Polymeric UV Absorber (Tinuvin 213) Using LDI-TOFMS: Solvent Effect in Sample Preparation

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The range of applications of polymeric materials is extending at an amazing rate and the number of additives available to modify polymer properties is increasing proportionately. These additives include antioxidants, UV stabilizers, lubricants, and so on. Polymeric materials undergo degradation when they are exposed to the ultraviolet (UV) radiation in sunlight. This degradation process results in a change in the appearance and reduction of the physical properties.

ortho-Hydroxyphenyl benzotriazoles are commonly used as UV absorbers (UVAs). They absorb potentially destructive UV radiation and dissipate the energy on a subpicosecond time scale.[1-6] The UVA is used to filter off UV radiation and dissipate the energy in the form of heat. UVAs must have a wide range of chemical and physical properties to be useful in applications, which include coatings and a wide variety of polymer products.[1] Tinuvin 213 is a mixture of polyethylene glycol (PEG) and two types of polymeric UVAs. It commonly applies to poly(methyl methacrylate) (PMMA), natural rubber (NR), thermoplastic elastomer (TPE), and so on. Chemical structures of the two UVAs are shown in Scheme 1. They are [3-[3-(2*H*-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]-hydroxypoly(oxo-1,2-ethanediyl) (CAS number: 104810-48-2) and 3-[3-(2*H*-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]-ω-[3-[3-(2*H*-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]-poly(oxy-1,2-ethanediyl) (CAS number: 104810-47-1), and for convenience they were named UVA_1 and UVA_2,
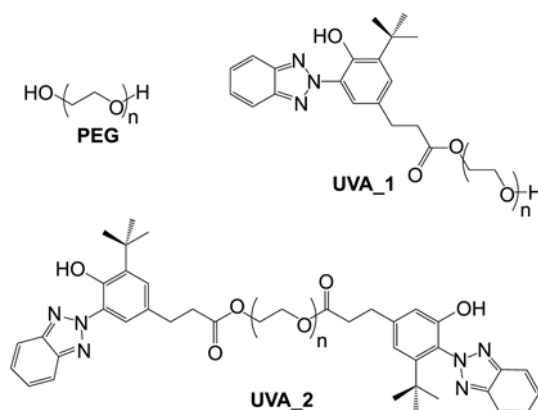
respectively. For the benzotriazole class UVAs, the mechanism of excited-state deactivation is thought to be due to an excited-state intramolecular proton transfer (Scheme 2).[1-7]

Analysis of polymer additives by mass spectrometry and its related techniques enhanced the capability of compound identification. Moving toward higher molecular weight additives with less volatility, conventional mass spectrometry techniques such as electron ionization (EI), chemical ionization (CI), and gas chromatography/mass spectrometry (GC/MS) are generally not suitable for their analysis. Thus soft ionization techniques such as field desorption, fast atom bombardment (FAB),[9,10] desorption chemical ionization (DCI),[11,12] laser desorption,[13-18] electrospray ionization (ESI),[19] and atmospheric pressure chemical ionization (APCI)[20,21] have been investigated for their utilities in the analysis of polymer additives either in polymer extracts or directly from polymer matrices.

Matrix-assisted laser desorption/ionization (MALDI) has been widely used as a soft ionization technique. And the absence of substantial fragmentation and the high sensitivity, combined with the theoretically unlimited mass range, make MALDI time-of-flight mass spectrometry (MALDI-TOFMS) a powerful tool for polymer characterization.[21-30] It can be used to determine average molecular weights and molecular weight distributions of narrow polydispersity polymers.[31] However, the success of this technique for polymer analysis is dependent on the sample preparation. Great care must be taken in developing sample preparation protocols to ensure the generation of accurate and precise results. Several studies have shown that a number of factors in sample preparation can affect the MALDI results.[22,32-37] Among them, the type and quality of solvents can greatly influence the MALDI analysis. It is demonstrated that sample morphology and polymer distribution on the probe can be greatly influenced by the type of solvents used.[38] For sample preparation in MALDI analysis of polymers, it is important to select a solvent system that will allow matrix crystallization to take

Scheme 1. Chemical structures of Tinuvin 213.
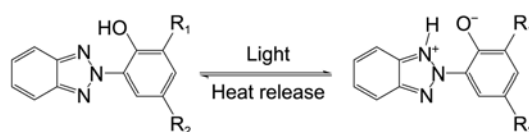
Scheme 2. UV absorption and energy dissipation of hydroxylphenyl benzotriazole UV absorber.

place prior to polymer precipitation. Brandt and coworkers[39] studied the solvent effect on ionization efficiencies of polystyrene and PEG, and reported that the signal-to-noise ratios were influenced by the kind of solvent.

The purpose of the present work is to examine whether change in solvent which used for sample preparation can affect the measurment of the average molecular weights of polymer and a role of UVAs as matrix. UV absorption spectrum of 50 ppm Tinuvin 213 in acetone was measured using UV-visible spectrometer to examine degree of the N_2 laser radiation (337 nm). Since the UVAs of Tinuvin 213 absorb UV wavelength between 295 and 400 nm (Figure 1), the two UVAs and PEG can be ionized without matrix by absorption of the laser radiation. We analyzed Tinuvin 213 using MALDI-TOFMS without any matrix (LDI-TOFMS). The absorbance of Tinuvin 213 at 337 nm is very high as shown in Figure 1. Figure 2 shows LDI mass spectrum of Tinuvin 213 dissolved in acetone. The sodiated molecules, $[M+Na]^+$, and potassiated molecules, $[M+K]^+$, of PEG, UVA_1, and UVA_2 of Tinuvin 213 were observed. The $[M+Na]^+$ peaks were marked in Figure 2. The $[M+K]^+$ peak was located at the right of the $[M+Na]^+$. Relative intensities of the $[M+Na]^+$ ions were much larger than those of the $[M+K]^+$ ions. The sodium and potassium cations are a ubiquitous contaminant
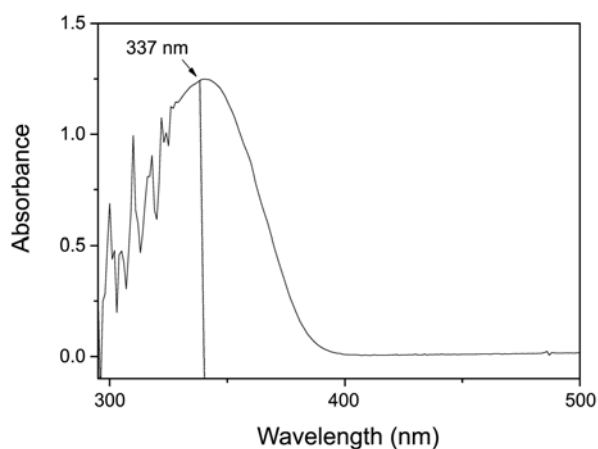

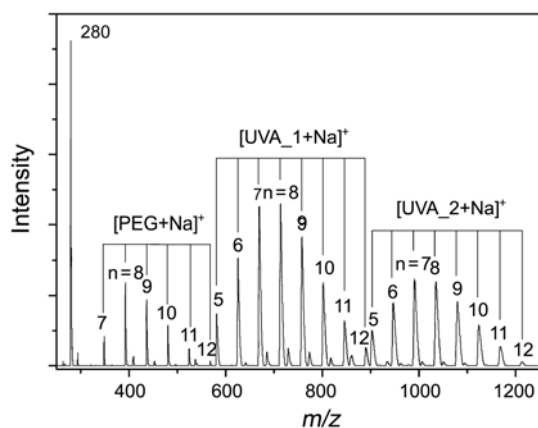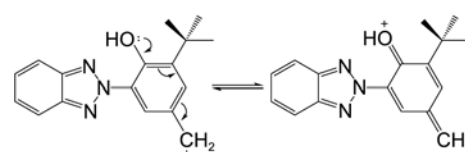**Figure 1.** UV spectrum of 50 ppm Tinuvin 213 in acetone.

Figure 2. LDI mass spectrum of 2000 ppm Tinuvin 213 dissolved in acetone.

Scheme 3. Structure and resonance of the *m/z* 280 fragment ion.

from glassware or moisture in the air. The *m/z* 349, 393, 437, 481, 525, and 569 were assigned to the $[PEG+Na]^+$ ions with n = 7, 8, 9, 10, 11, and 12, respectively. The *m/z* 582, 626, 670, 714, 758, 802, 846, and 890 were assigned to the $[UVA\_1+Na]^+$ ions with n = 5, 6, 7, 8, 9, 10, 11, and 12, respectively. The *m/z* 903, 947, 991, 1035, 1079, 1123, 1167, and 1211 were assigned to the $[UVA\_2+Na]^+$ ions with n = 5, 6, 7, 8, 9, 10, 11, and 12, respectively. The mass difference was $\Delta m/z$ 44 (CH_2CH_2O). Tinuvin 213 was successfully analyzed without any matrix. This is because the UVA_1 and UVA_2 strongly absorb the laser radiation of 337 nm. The UVA_1 and UVA_2 were desorbed from the sample plate and ionized by absorption of 337 nm. PEG was also desorbed and ionized by assistance of the UVA_1 and UVA_2. Hence, the UVA_1 and UVA_2 played a role as matrix for desorption and ionization of PEG.

In addition to the sodiated and potassiated molecules, one fragment ion of *m/z* 280 was also observed as shown in Figure 2. The *m/z* 280 fragment ion was formed from both UVA_1 and UVA_2. The fragment ion can be formed by dissociation of ~CH_2-CH_2~ bond of the UVA_1 and UVA_2, and it may have a stable resonance form as shown in Scheme 3. Detection of the fragment ion is very interesting because MALDI is a soft ionization method. It can be considered that the UVAs have excess internal energy enough to dissociate the carbon-carbon bond of the UVA_1 and UVA_2 by direct absorption of the UV radiation. The UVAs absorb 337 nm and dissipate the energy in the form of heat to generate a thermally excited species. The *m/z* 280 fragment ion is very important clue for the identification of Tinuvin 213.

From the LDI mass spectra, average molecular weights of the PEG, UVA_1, and UVA_2 were calculated by the equations (1) and (2).

$$M_n = \Sigma_i m_i N_i / \Sigma_i N_i \qquad (1)$$

$$M_w = \Sigma_i m_i^2 N_i / \Sigma_i m_i N_i \qquad (2)$$

where M_n is the number average molecular weight, M_w is the weight average molecular weight, m_i is the molecular weight of the i-th fraction, and N_i is the number of molecules of the m_i. The average molecular weights were plotted as a function of the dielectric constant of the solvent. Dielectric constants (ε) of methylene chloride, acetone, ethanol, and methanol are 9.08, 20.7, 24.30, and 32.63, respectively. Figures 3, 4, and 5 show the variations of the M_n and M_w of PEG, UVA_1, and UVA_2 with the dielectric constant of solvent, respectively. By increasing the dielectric constant, the average molecular weights of PEG, UVA_1, and UVA_2 on the whole increased. This can be explained with the
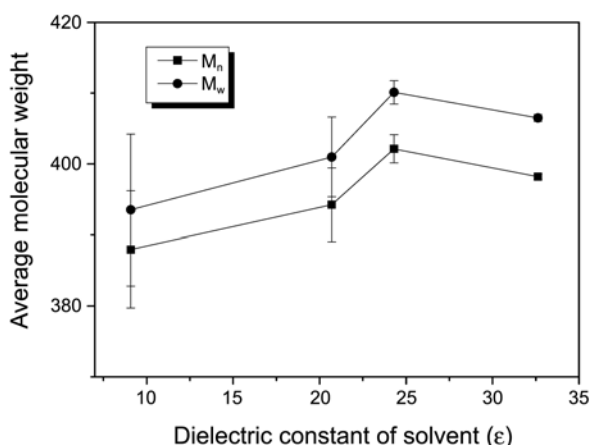
Notes

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Figure 3. Variation of the average molecular weights of PEG with the dielectric constant of solvent. Squares and circles denote the number and weight average molecular weights, respectively.

Figure 4. Variation of the average molecular weights of UVA_1 with the dielectric constant of solvent. Squares and circles denote the number and weight average molecular weights, respectively.
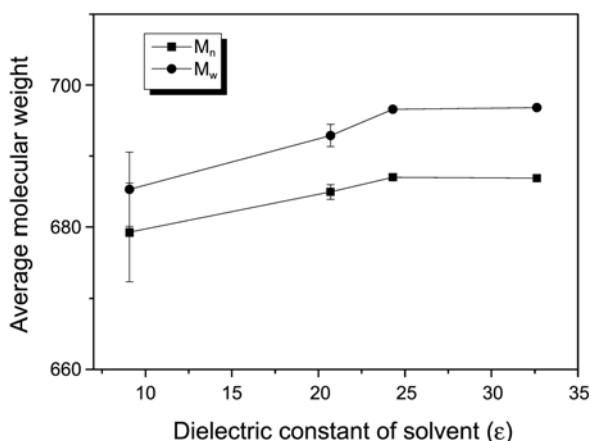

Figure 5. Variation of the average molecular weights of UVA_2 with the dielectric constant of solvent. Squares and circles denote the number and weight average molecular weights, respectively.
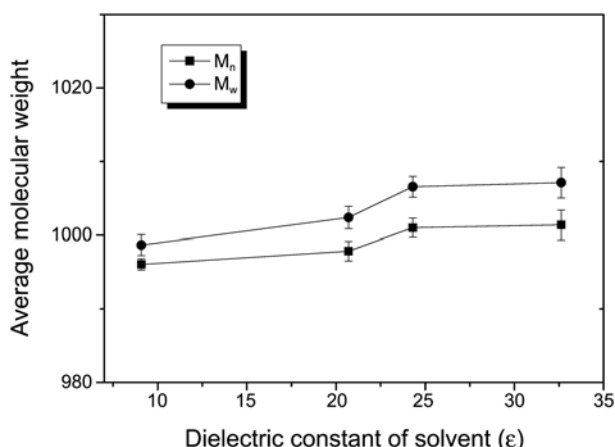
conformations of molecules of the PEG, UVA_1, and UVA_2. Polymer precipitation competes during the drying of the sample solution on the MALDI sample plate. Conformation

of polymer may be dependent on the compatibility with the solvent. When chemical compatibility between polymer and solvent is very good, the polymer may have unfolded structure by good intermolecular interactions between polymer and solvent. If not, the polymer may have some folded structure. In general, the unfolded structure of a molecule has larger volume than the folded one and the number of molecules contacted with the unfolded polymer is also larger than that with the folded one. And dielectric constant of a polymeric material decreases as the molecular weight increases. Dielectric constants of PEG 200 (average molecular weight 200 g·mol^{-1}), PEG 300 (300 g·mol^{-1}), PEG 400 (400 g·mol^{-1}), and PEG 600 (600 g·mol^{-1}) at 25 $^{\circ}$C are 22.1, 19.2, 17.3, and 14.3, respectively.[40] A polymeric material with higher molecular weight may have relatively more folded structure than that with lower one in solvent. And the analyte molecules may have more folded structures in solvent with higher dielectric constant than in solvent with lower dielectric constant. A folded structure molecule can be more easily desorbed from the sample plate than an unfolded one. Hence, molecular weight distributions of the analytes obtained using MALDI-MS analysis may shift to larger value as the dielectric constant of solvent increases.

Polydispersity index (PDI, M_w/M_n) was also calculated to investigate the variation of PDI with the solvent polarity. PDIs of the PEG were 1.014, 1.017, 1.020, and 1.021 for the solvents of methylene chloride ($\varepsilon = 9.08$), acetone ($\varepsilon = 20.7$), ethanol ($\varepsilon = 24.30$), and methanol ($\varepsilon = 32.63$), respectively. PDIs of the UVA_1 were 1.009, 1.012, 1.014, and 1.014, respectively, while those of the UVA_2 were 1.003, 1.005, 1.006, and 1.006, respectively. PDI was also slightly increased as the dielectric constant of solvent increased. This also means that ions with higher mass were detected more than those with lower one. This may be also due to the molecular structures of analytes as discussed previously. In conclusion, compatibility of the solvent with the analyte molecule may affect the morphology of the analyte molecule and the desorption/ionization behaviors according to the molecular weights.

Experimental Section

The Tinuvin 213 was purchased from Ciba Co. HPLC grades of methanol, ethanol, acetone, and methylene chloride were purchased from J. T. Baker Co. and were used as the solvent for sample preparation. The Tinuvin 213 was dissolved in the solvent to make 2000 ppm. The analyte solution of 1.0 μL was spotted on the sample plate and dried in the air.

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

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