Influence of Fragmentor Voltage and Solvent on Negative Ionization Behaviors of Uvinul 3039 Using LC/APCI-MS

Sung-Seen Choi* **and Min Ju Song**

*Department of Chemistry, Sejong University, Seoul 143-747, Korea. *E-mail: sschoi@sejong.ac.kr*
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Engineering plastics undergo degradation when exposed to the ultraviolet radiation in sunlight. This degradation process results in appearance changes such as discoloration, chalking, and crazing as well as reduction of physical properties. UV absorbers slow down the degradation process by absorbing harmful ultraviolet radiation and dissipating it as thermal energy. Analysis of UV absorbers is very important to understand polymer degradation studies and quality-assurance testing. 2-Ethylhexyl-2-cyano-3,3-diphenylacrylate (Uvinul 3039) is one of popular cyanoacrylate UV absorbers since it is aprotic and stable UV absorber. Uvinul 3039 has a single absorption band with a maximum at 305 nm.

Analysis of UV absorbers is difficult because of requirement of a sensitive method for identification, high molecular weight, and high polarity. Thus, gas chromatography (GC) is not suitable for analysis of UV absorbers. Although high performance liquid chromatography (HPLC) with UV detection has been successfully used, this method is only applicable to compounds having UV-absorbable groups. These problems can be solved by the use of liquid chromatography/mass spectrometry (LC/MS),[1,2] especially LC/MS with atmospheric pressure chemical ionization (LC/APCI-MS)[3]. Block and coworkers[3] analyzed antioxidants and UV stabilizers for polymeric materials using LC/APCI-MS. In APCI, a corona discharge makes solvent reactant ions that are used to ionize the sample by chemical ionization. Solute and sample are vaporized by pneumatic nebulization. APCI relies upon gas-phase ion-molecule reactions to place a charge on neutral analytes, so it is especially important to understand these reactions. Kostiainen and Bruins reported that a judicious selection of solvent can be made to promote ionization of the compound of interest.[4-7] When mobile phase transports analyte molecules. APCI can deliver a proton to the analyte. The solvent-derived ions serve as reagents for proton transfer ionization.

Mass spectrometry with APCI gives a great deal of structural information in a short analysis time. In APCI-MS, fragmentation pattern can be obtained by varying the fragmentor voltage (or accelerating voltage) and some fragment ions are produced to identify the structure of an analyte.[8] A key parameter in tuning the instrument's sensitivity is the fragmentor voltage (similar to cone voltage in other instruments). At higher fragmentor voltage settings, collision-induced dissociation (CID) can be initiated in the region between the end of the transfer capillary and the first skimmer cone, so that fragmentation increases.[9] In this study, we analyzed Uvinul 3039 using LC/APCI-MS with negative ion mode and investigated the ionization behaviors such as formation of solvent-adducted ion and fragmentation by varying the fragmentor voltage and kind of solvent. Methanol, ethanol, and acetone were employed as the solvent and eluent. These solvents have been used for extraction of organic additives including UV absorbers from plastic polymers such as polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), and poly(vinyl chloride) (PVC).[10,11]

Figure 1 shows the mass spectra of Uvinul 3039 in methanol, ethanol, and acetone at the fragmentor voltage of 160 V. Molecular ion, M^- (m/z 361) was observed along with the solvated molecule, $[M + solvent - H]^-$. Formation

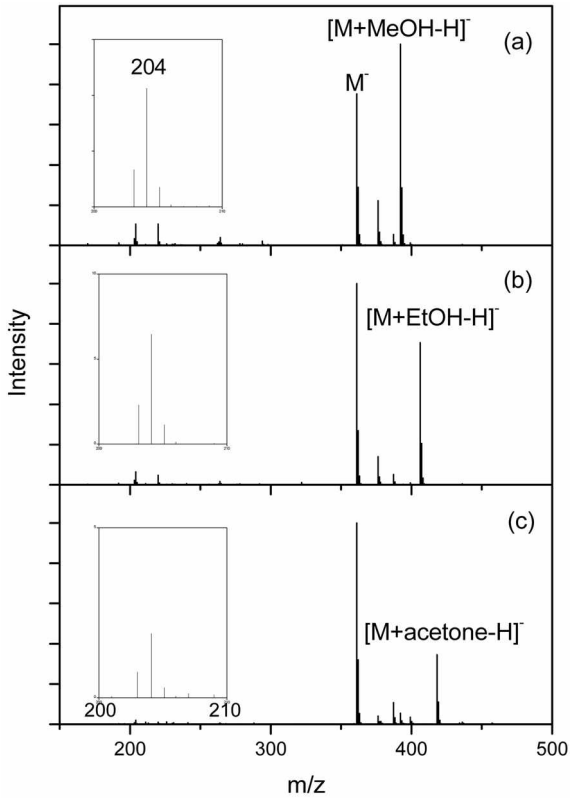


Figure 1. Mass spectra of Uvinul 3039 at the fragmentor voltage of 160 V using methanol (a), ethanol (b), and acetone (c) as the solvent and eluent.

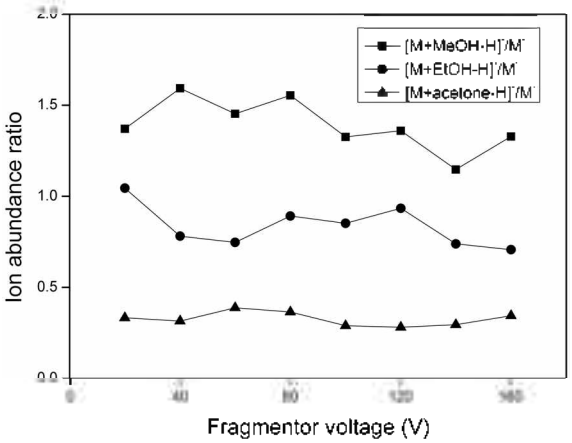


Figure 2. Variation of the intensity ratio of $[M + solvent - H]^-/M^-$ of Uvinul 3039 with the fragmentor voltage. Squares, circles, and triangles stand for methanol, ethanol, and acetone used as the solvent and eluent, respectively.

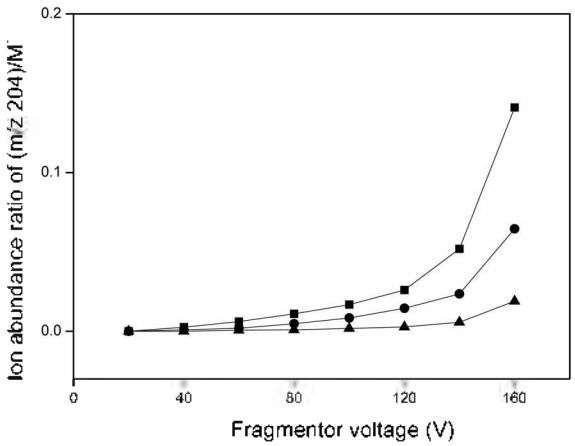
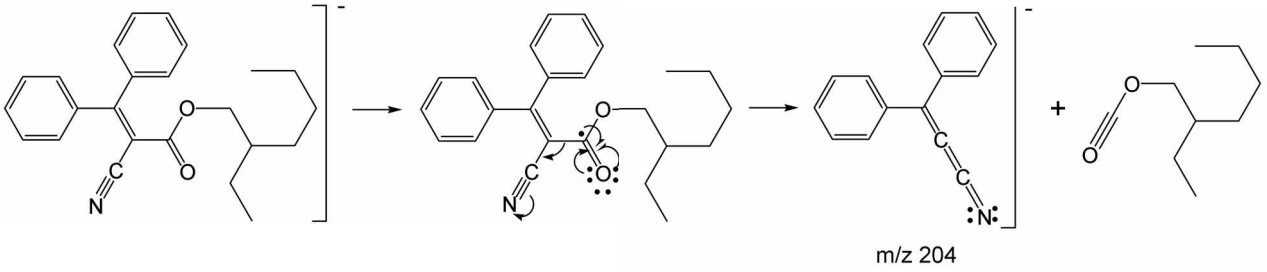


Figure 3. Variation of the ion intensity ratio of $(m/z\ 204)/M^-$ of Uvinul 3039 with the fragmentor voltage. Squares, circles, and triangles stand for methanol, ethanol, and acetone used as solvent and eluent, respectively.

of the M^- not the $[M - H]^-$ may be because Uvinul 3039 is an aprotic species. Ion abundance of the [M + methanol − H]⁻ is larger than that of the M^- whereas those of the [M + ethanol − H]⁻ and [M + acetone − H]⁻ are smaller than that of the M^-. For Uvinul 3039 in methanol and ethanol, relative ion abundance of the M^- tends to increase with increasing the fragmentor voltage compared to the [M + solvent − H]⁻. This is due to desolvation by the increased collision energy. In order to investigate the influence of the fragmentor voltage on the ion abundance ratio of [M + solvent − H]⁻/M⁻, the [M + solvent − H]⁻/M⁻ ratio was plotted as a function of the fragmentor voltage as shown in Figure 2. The [M + methanol − H]⁻/M⁻ and [M + ethanol − H]⁻/M⁻ ratios slightly decrease with increasing the fragmentor voltage. However, the [M + acetone − H]⁻/M⁻ ratio almost does not vary with the fragmentor voltage. This implies that formation of the M^- in acetone is accomplished through intermolecular charge transfer reaction between acetone anion and the analyte not intramolecular ion-molecule reaction of the [M + acetone − H]⁻. The [M + acetone − H]⁻/M⁻ ratio is much smaller than the [M + methanol − H]⁻/M⁻ and [M + ethanol − H]⁻/M⁻ ones. This can be explained with the steric hindrance and stability of the [solvent − H]⁻. The 2-ethylhexyl of Uvinul 3039 can prevent the [solvent − H]⁻ from binding to neutral Uvinul 3039 molecule since it is a relatively long chain. When the solvent molecule size is big, the steric hindrance effect occurs well. The order of solvent molecule size is acetone > ethanol > methanol. Another possible reason is stability of the [solvent − H]⁻ such as CH_3O^-, $CH_3CH_2O^-$, and CH_3-C(=O)-CH_2^-. CH_3-C(=O)-CH_2^- is more stable than CH_3O^- and $CH_3CH_2O^-$ because it has resonance stricture of CH_3-C(-O⁻)=CH_2. Reaction capability to form the [M + solvent − H]⁻ will be reduced by increasing the stability of the [solvent − H]⁻.

At high fragmentor voltage, fragment ion of the m/z 204 was observed irrespective of the solvents as shown in Figure 1. This is very interesting because APCI is soft ionization method. The m/z 204 can be formed from the molecular ion by loss of $C_4H_9(C_2H_5)CH_2$-O-CO as shown in Scheme 1. The $(m/z\ 204)/M^-$ ratio continuously increases as the fragmentor voltage increases irrespective of the kind of solvents. The $(m/z\ 204)/M^-$ ratio slightly increases until 120 V of the fragmentor voltage and then strikingly increases as shown in Figure 3. The $(m/z\ 204)/M^-$ ratios of methanol are larger than the others and those of ethanol are larger than those of acetone. Difference in the $(m/z\ 204)/M^-$ ratios according to the kind of solvents can be explained with the collision frequency. Formation of the m/z 204 ion will be activated by enhancing the collision energy. The collision energy is increased by increasing collision frequency as well as by increasing the fragmentor voltage. When the M^- moves from the ion source to the detector, it collides with neutral solvent molecules. Thus, collision frequency will be increased by increasing the number of neutral solvent molecules existing



Scheme 1. Fragmentation mechanism of M^- of Uvinul 3039.

in the pathway of the M^-. Densities of methanol, ethanol, and acetone at room temperature are 0.79, 0.79, and 0.87, respectively, and their molecular weights are 32, 46, and 58 g/mol, respectively. When the liquid solvents of the same volume are vaporized, ratios of the number of molecules are 1.0, 0.69, and 0.61 for methanol, ethanol, and acetone, respectively.

From the experimental results, we can lead to a conclusion as follow: the $[M + solvent - H]^-$ of Uvinul 3039 is generated besides the M^-, the $[M + methanol - H]^-/M^-$ and $[M + ethanol - H]^-/M^-$ ratios are larger than the $[M + acetone - H]^-/M^-$ one, and formation of the fragment ion of m/z 204 is able to do the structural analysis of Uvinul 3039 in negative APCI. It was also found that the negative ion mode generated simpler fragmentation pattern than the positive ion mode.

Experimental Section

Uvinul 3039 was purchased from Aldrich Chemical Co. and used as received without further purification. All solvents used were high performance liquid chromatography (HPLC) grade purchased from JT Baker Co. 1000 ppm solutions were prepared by dissolving Uvinul 3039 in methanol, ethanol, and acetone.

LC/APCI-MS of HPLC 1200 instrument coupled to a single quadrupole LC-MS 6130 mass spectrometer of Agilent Technologies Inc was used. The liquid chromatograph used a binary pump and an injection valve with a 10 μL sample loop. A sample of 10 μL was introduced by means of a Rheodyne valve. The eluent was the same solvent and the flow rate was 1.0 mL/min. MS detection was achieved using a single quadrupole spectrometer equipped with an APCI ionization source. The following instrumental parameters were used for the LC/APCI-MS analysis in the negative ion mode: capillary, 4 kV; fragmentor voltage, 20, 40, 60, 80, 100, 120, 140, 160 V; corona current, 4.0 μA; quardrupole temperature, 100 °C; vaporizer temperature, 325 °C.

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