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Effect of Cation Complexation of Hindered Phenol Antioxidants on their Fragmentation in Electrospray Ionization Tandem Mass Spectrometry

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Abstract : The fragmentation pattern of four hindered phenol antioxidants was investigated using ammonium and lithium ions as the additives for ionization. Due to different binding geometries and interactions, they underwent different characteristic fragmentation reactions providing useful complementary information for structural analysis of hindered phenol antioxidants. Ammonium ion adducts were fragmented successively until all *t*-butyl groups were lost in the form of isobutylene and allowed the estimation of the number of *t*-butyl groups present in the molecule. Lithium ion adducts produced fragment ions from major backbone cleavage, on the other hand, which provide more crucial information for the identification of detailed backbone structure.

Keywords : hindered phenol antioxidant, fragmentation, ammonium ion adduct, lithium ion adduct

Introduction

Antioxidants are blended in various synthetic polymers to enhance long-term stability of polymer products against oxidative and thermal degradation.[1,2] Especially the hindered phenolic compounds have been extensively used due to their excellent antioxidant activities with a small amount.[2,3] They work by donating their phenolic hydrogen to scavange free radicals generated in a polymer material. Residual phenoxy radicals are resonance-stabilized with additional protection by sterically hindering funcational groups.

Mass spectrometric analysis of relatively non-polar and thermall labile polymer additive, including antioxidants and photo-stabilizers, is not trivial due to low ionization efficiency and undesirable chemical reactions during ionization. Particularly in electrospray ionization (ESI), protonation is not generally favorable compared to other cation adduct formation, including Li^+, NH_4^+, Na^+, K^+ adducts. Many non-polar additives are also observed as the cation adducts in ESI, where as protonated molecules are rarely observed.[4] The differences in binding geometry and stength of cations with polymer additives affect their bond strengths, and often resulted in different fragmentation behaviors in tandem mass spectrometry.

Here, four hindered phenol antioxidants widely used in polymer products were analyzed by ESI mass spectrometry (MS). The differences in fragmentation behaviors of antioxidants complexed with ammonium and lithum ion were investigated and its implication on the structural analysis of polymer additves was discussed.

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This Article is dedicated to Professor Seung Koo Shin in commemorating his retirement and contribution to the Korean Society for Mass Spectrometry.

Experimental

Materials and reagents

Four hindered phenol antioxidants (Nugard XL-1, Irganox 245, Irganox 1076, Irganox 1010) were obtained from LG Chemical Co. Ltd. (Daejeon, Korea). Methanol, tetrahydrofuran, ammonium acetate and lithium chloride were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Electrospray ionization tandem mass spectrometry

For mass spectrometric analysis of hindered phenol antioxidants, a Finnigan LCQ ion trap mass spectrometer (MS) equipped with electrospray ionization (ESI) interface was used. Electrospray voltage of 3.5 kV was used with nitrogen nebulization gas. The temperature of the heated

capillary was maintained at 200°C. The precursor ions were isolated using tailored waveform at q_z = 0.83, while ion excitation for ion fragementation was carried out at q_z = 0.25 for 30 ms with amplitude adjusted for optimum efficiency of collision-induced dissociation (CID). The ion trap mass analyzer was filled with 1-2 mtorr of He gas for ion cooling and CID. For each antioxidant, 0.1 mM sample solution was prepared in 1:1 mixture of methanol and tetrahydrofuran containing 0.5 mM ammonium acetate to produce $[M+NH_4]^+$ molecular ion in ESI. To generate $[M+Li]^+$ molecular ion 0.5 mM lithium chloride was used instead of ammonium acetate. Each sample soluition was infused into the electrospray needle with flow rate of 50 μL/min.

Results and Discussion

Electrospray ionization of hindered phenol antioxidants

The chemical structures and nomimal molecular masses of four commonly used hindered phenol antioxidants investigated in this study are shown in Figure 1. Infusion of these compounds doesn't make protonated molecule, $[M+H]^+$, but typically produces alkali ion adduct, often utilizing trace amount of alkali metal ions in solvent. For stable generation of molecular ion, the sample solution for each compound was prepared as a mixture with ammonium acetate or lithium chloride. Although ESI doesn't generate $[M+H]^+$ efficiently due to lack of basic functional groups, strong and dominant $[M+NH_4]^+$ and $[M+Li]^+$ molecular ions can be observed in the presence of ammonium and lithium ions, respectively.

Fragmentation of ammonium ion adduct of hindered phenol antioxidants

Hindered phenol antioxidants typically have many *t*-butyl functional groups on ortho position of the phenolic group to provide steric protection. The characteristic fragmentation for ammonium ion adducts of those antioxidants was facile and successive losses of *t*-butyl group (in the form of isobutylene) until all *t*-butyl groups were lost as shown in Figure 2. $[M+NH_4]^+$ of Nugard XL-1 at *m/z* 714 produced *m/z* 585, 529 and 473 as the major fragments. Fragment ion at *m/z* 585 corresponds to two succesive loss of *t*-buyl groups after loss of NH_3. Losses of remaining *t*-butyl groups generated ions with *m/z* 529 and 473. Although a backbone cleavage was also observed at *m/z* 307, its abundance was almost negligible. In the case of Irganox 1010, the same fragmentation pattern was observed (Figure 3). The major fragmentation pathway of $[M+NH_4]^+$ at *m/z* 1194 for Irganox 1010 was also the successive losses of eight *t*-butyl group after loss of NH_3, which produced *m/z* 953, 897, 841, 785 and 729. A series of ions with lower abundance was additionally observed at *m/z* 899, 843, 787, 731, 675, 619 and 563. After the fragment ion at *m/z* 899 was generated from NH_3 loss and ester backbone cleavage, successive losses of *t*-butyl groups made the series of ions.

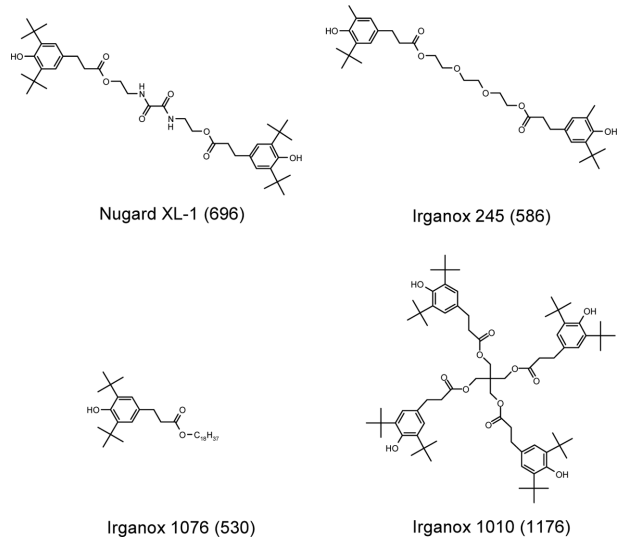

Figure 1. Four hindered phenol antioxidants investigated in this study.

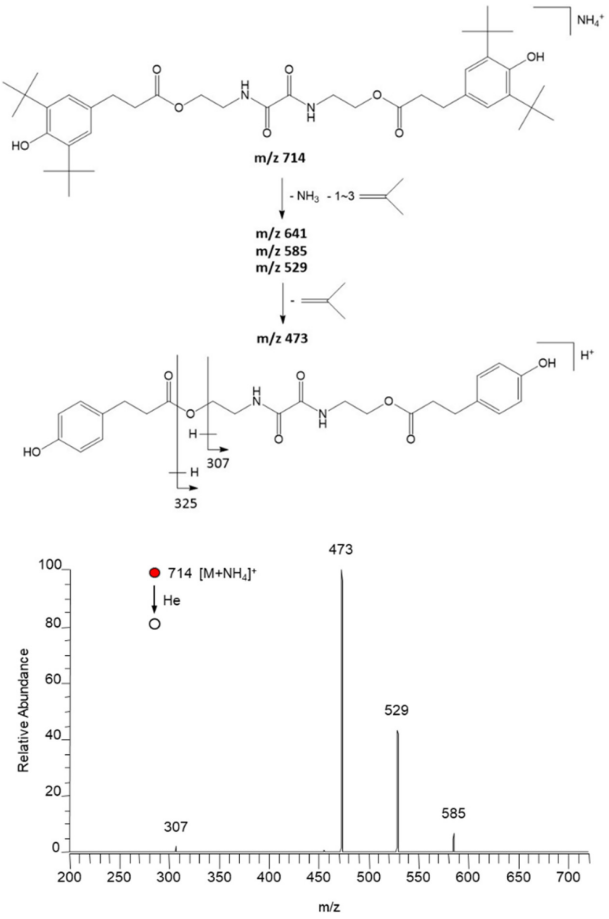

Figure 2. Fragmentation of ammonium ion adduct of Nugard XL-1.

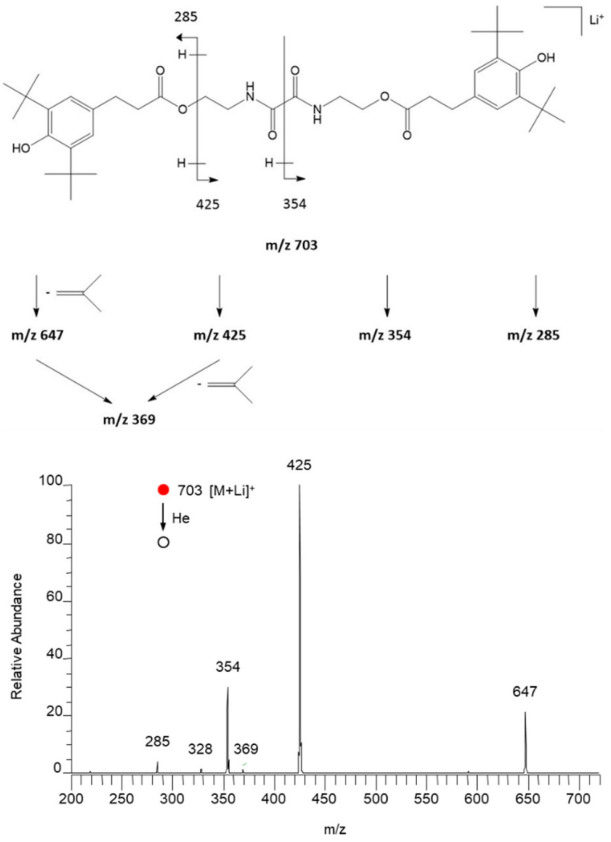

Figure 3. Fragmentation of lithium ion adduct of Nugard XL-1.

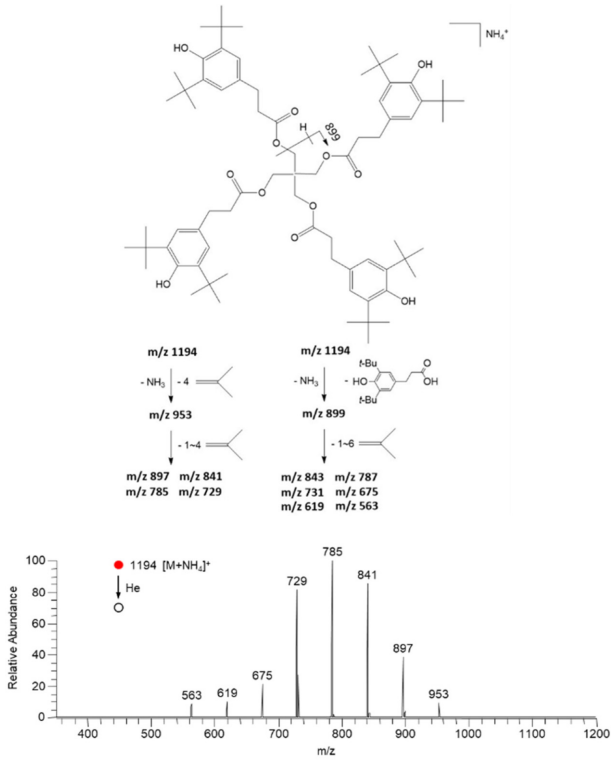

Figure 4. Fragmentation of ammonium ion adduct of Irganox 1010.

Fragmentation of lithium ion adduct of hindered phenol antioxidants

It is generally known that cationization of relatively non-polar molecules with ether, ester and alcholic functional groups requires higher collision energy for fragmentation compared with protonated molecules. Among alkali metal ions, lithium ion adduct is known to be fragmented at relatively lower collision energy. Lithium ion adduct of Nugard XL-1 at *m/z* 703 produced fragment ions easily at low collision energy as predicted, but its pattern was remarkably different from that of ammonium ion adduct (Figure 4). Although a single loss of *t*-butyl group was observed at *m/z* 647, the major fragment ions at *m/z* 425 and 354 were due to backbone cleavages. The MS/MS of lithium ion adduct at *m/z* 1183 for Irganox 1010 also showed backbone cleavages as the major fragmentation pathway with no loss of *t*-butyl groups. As shown in Figure 5, *m/z* 905 was formed by the cleavage of ester group and the loss of a 3.5-di-*t*-butyl-4-hydroxyhydrocinnamic acid. Subsequent losses of two 3,5-di-*t*-butyl-4-quinone methide groups produced ions at *m/z* 687 and 469, respectively. A minor fragmentation pathway at *m/z* 899 and 681 is due to loss of lithium salt of 3.5-di-*t*-butyl-4-hydroxyhydrocinnamic acid, followed by loss of 3,5-di-*t*-butyl-4-quinone methide group.

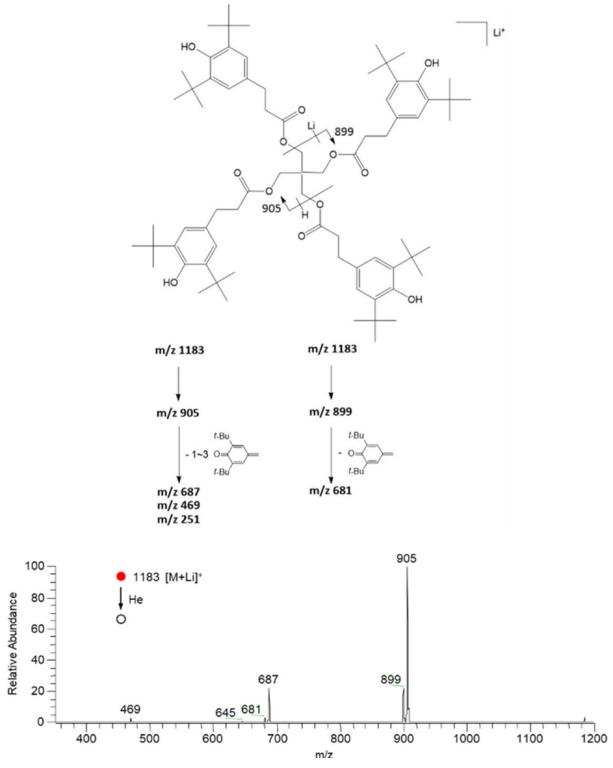

Figure 5. Fragmentation of lithium ion adduct of Irganox 1010.

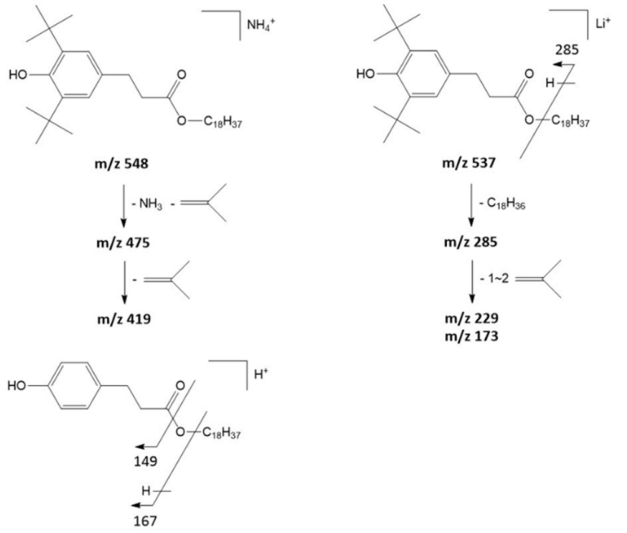

Figure 6. Fragmentation of ammonium and lithium ion adducts of Irganox 1076.

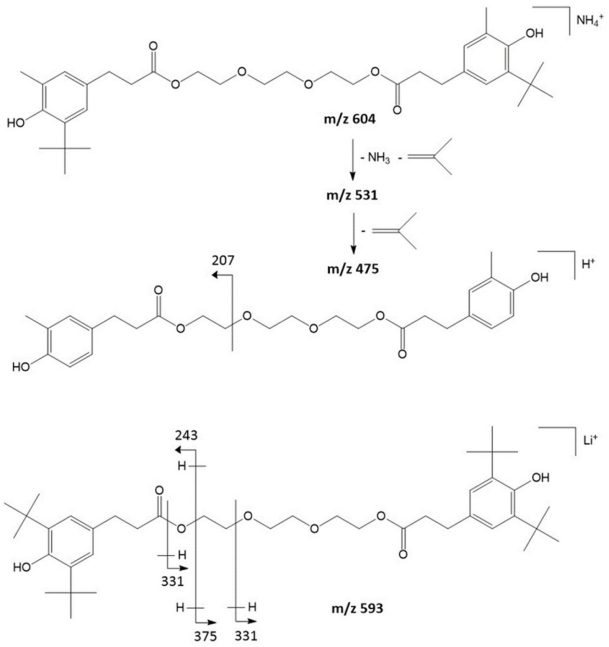

Figure 7. Fragmentation of ammonium and lithium ion adducts of Irganox 245.

Effect of ammonium and lithium ion adduction on the fragementation of hindered phenol antioxidants

The fragmentation of ammonium and lithium ion adducts for Irganox 1076 and Irganox 245 was also observed. Their fragmentation showed almost the same trend as those of Nugard XL-1 and Irganox 1010. As shown in Figure 6 and 7, fragmentation of ammonium adduct ions produced series of ions corrsponds to succesive of *t*-butyl group, while that of lithium adduct ions showed the backbone cleavages at ester or ether group as the major fragmenation pathway. The fragmentations of lithium ion adducs provide rich structural information for hindered phenol antioxidants, because they come from major backbone cleavages. In constrast, those of ammonium ion adducts looks not so informative. However, it also provides complementary information for structural analysis when it is used with the fragmentations of lithium ion adducts. In a favorable case, information on the number of *t*-butyl group present in a molecule can be obtained as well.

Conclusions

The fragmentation patterns of ammonium and lithium ion adducts of hindered phenol antioxidants were investigated. Facile loss of *t*-butyl groups was dominantly observed for low energy CID of $[M+NH_4]^+$, which is not so informative for the characterization of backbone structure of a compound in this class. Notwithstanding, it provides information on the number of *t*-butyl groups present in the molecule in a favorable condition. For CID of $[M+Li]^+$, ester/ether backbone cleavages were the major fragmentation pathway, which are very useful for the identification of detailed backbone structure. Efficient binding of Li^+ to several ether and/or ester oxygens seems to induce ester/ether backbone cleavages. The present method can be applied to MS/MS & LC-MS/MS analyses of polymer additives taking advantage of various cation with different binding properties.

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