Introduction

Mass spectrometric methods are extensively used for over a hundred years. Several scientific discoveries have been achieved by using mass spectrometry. Some of these: discovery of isotopes, precise determination of atomic masses, discovery of new elements, quantitative gas analysis, quick detection of trace amount of contaminants, fast detection of pharmaceutical products, quick and precise determination of the chemical structure.

Due to the improvement occurred in mass spectrometry during the past years the method has become one of the most effective techniques used for determination of material composition and structure.

Intensive research is still in progress these days in order to construct small and compact mass spectrometers. Efforts are taken also to find additional ionization techniques. MALDI (Matrix-Assisted Laser Desorption/Ionization) and ESI (ElectroSpray Ionization) ionization techniques enable the complex structural investigation of synthetic systems and nonvolatile biopolymers of high molecular weights.

A modern Bruker-typed MALDI-TOF MS instrument was installed at the Department of Applied Chemistry of the University of Debrecen in 2000. The installation of a new Bruker-type ESI-TOF MS instrument ensured the technical background of further investigations. Since than several chemical problems and unknown reaction mechanism concerning polymer systems were revealed.

This gave rise to study different chemical systems by MALDI-TOF MS and „post-source decay" (PSD) MALDI-TOF MS/MS. The obtained results provide information about the cationization and its mechanism under MALDI conditions.

Study of cationization is of great importance from analytical point of view. In order to get valuable spectrum by MALDI MS an adduct ion ($[M+Cat]^+$) should be generated from the sample and a cation. In the majority of cases the cation is proton (H^+) or alkali metal ion for example sodium or potassium ion. The process of ion fragmentation, which is dependent on the quality of the cation forming the adduct ion,

and the stability of the adduct ion (cation + sample interaction) have significant effect on the quality of the obtained MALDI spectrum.

This dissertation represents the application of MALDI-TOF MS and PSD MALDI-TOF MS/MS for different chemical systems and study of chemical structures, fragmentation reaction mechanisms and thermodynamics based on the obtained information. The dissertation consists of three main parts. The first part contains observations gained during investigation of polystyrene cationized by silver ions. The second part contains fragmentation analysis of compounds having low molecular weight (in this case plasticizers). The last part represents the effect of different alkali metal ions on the cationization of PEG4000 and PEG6000 polymers.

I. Applied materials and instruments, sample preparation

I.1. Materials

During investigations reference materials of low molecular weight were represented by plasticizers, several of which were commonly used adipate and phthalate ester-typed plasticizers, for example di-octyl-adipate or di-izononyl-phtalate. Some polar and apolar polymers having different molecular masses [poly(ethylene glycol) and polystyrene] were also investigated by mass spectrometry.

More than ten routinely used matrices were applied for the MALDI-TOF MS and PSD MALDI-TOF MS/MS experiments, for example 1,8,9-Trihydroxy-antracene (ditranol, DIT) or 2,5-Dihydroxy-benzoic acid (2,5-DHB). Chloride salts of alkali metal ions and silver trifluoro acetate were selected as cationizing agent.

I.2. Instruments and softwares

MALDI MS and PSD MALDI MS/MS experiments were performed by a Bruker BIFLEX III^{TM} typed mass spectrometer equipped with a time-of-flight (TOF) mass analyzator and a reflectron. The obtained spectra were evaluated by a Bruker XMASS 5.0 software. The PSD spectra were calibrated by Adrenocorticotropic Hormone (ACTH). Infrared measurements were carried out on a Perkin Elmer Paragon

1000 PC type Fourier-transformation spectrometer. Gas chromatographic measurements were performed on a HP 5890 II instrument.

For the fitting of different distributions the Gauss-Newton-Marquard procedure of FITTER 5v program was used.

I.3. Sample preparation

The sample preparations followed almost the same pattern in every case. We separately dissolved the matrix, the analyte and the ionization agent, if it was necessary. Then specific amounts of the solutions were mixed. A volume of some mL of the solution was deposited onto a metal sample plate and allowed to air-dry before introducing it into the MS instrument.

II. New scientific results

II.1. Preparation of high aggregation silver clusterions under MALDI conditions

Positively and negatively charged silver-cluster ions were effectively produced under MALDI conditions up to the aggregation number of n ≅ 200, using reductive polar organic matrices and silver trifluoroacetate (AgTFA).

It was found that the matrix greatly influences the resulting cluster ion abundances. The effect of matrices with various chemical structure on the cluster formation was systematically investigated. It was also observed that the ion intensities decreased sharply at particular cluster numbers called ‘magic’ numbers, independently of the matrix used. Odd-even oscillations in the ion intensity and the magic numbers predicted by the jellium model theory were observed irrespectively of the matrix used.

Strong cluster ion signals were produced with matrices containing carboxyl group, but among these matrices HABA [2-(4-hydroxyphenylazo)benzoic acid] yield the most abundant cluster ions. The highest observable magic numbers in this work are 139 and 137 for Ag_n^+ and Ag_n^- cluster ions, respectively. The mixture of HABA and AgTFA proved to be an effective source of cluster ions in MALDI, which can be utilized by mass selection of specific size for the study of cluster ion-molecule reactions and/or fabricating nanodevices.

On the other hand, however, when the analysis of nonpolar polymers with silver ion cationization are in the focus, application of such matrices is disadvantageous due to the extensive cluster ion formation. Based on the experimental results it can be concluded that excited matrix molecules reduce the silver ions most probably *via* adduct ions. It is also reasonable to assume that the matrix can act as a „carrier gas" enhancing the growth of the clusters.

The fragmentation behaviors of different cluster ions under MALDI conditions are in line with those experienced by other methods.

II.2. The effect of the cationization on the fragmentation of compounds with low molecular weight

Fragmentation behaviors of compounds having low molecular weight were investigated. The commonly used PVC plasticizers were selected to represent such compounds. Detection and structural analysis of different PVC plasticizers were performed by MALDI-TOF MS and PSD MALDI-TOF MS/MS.

We concluded that MALDI-TOF MS and PSD MALDI-TOF MS/MS are capable to detect not only compounds with high molecular weight, but detect such compounds having relatively low molecular weight.

The PSD MALDI-TOF MS/MS spectra obtained by different methods of plasticizers cationized by proton and sodium ion were compared.

It is also revealed that the adduct ions cationized by proton formed more fragments than that of the sodium ion, thus according to get as many information as we can concerning the chemical structure we need to use the protonated adduct ions.

A novel method was introduced to determine the chemical structure of plasticizers form the PVC samples without extraction.

II.3. The effect of cationization on the molarmass distribution of polymers

In order to understand the effect of ion pairs on ionization processes the effect of several alkali metal ions and their mixtures on different polymer systems was investigated. To study cationization and its selectivity the effect of all the five alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) on the MALDI-TOF MS and PSD MALDI-TOF

MS/MS spectra of PEG4000 (M = 4000 g/mol) and PEG6000 (M = 6000 g/mol) reference polymers were investigated.

Relationship was found between the signal intensity ($\Sigma I_{Pn,Na+}/\Sigma I_{Pn,C+}$) and the concentration ratio ($[Na^+]_o/[C^+]_o$).

A new selectivity parameter, α, was introduced in order to characterize the selectivity of different alkali metal ions related to sodium ion. The advantage of this new selectivity parameter is that it accurately characterizes the interactions between metal ions and polymers in wide alkali metal ion concentration ranges.

It was also concluded that the dependence of signal intensities in the MALDI-TOF MS spectra of poly(ethylene glycols) cationized by different types of alkali metal ions on the PEG degree of polymerization shows Poisson-type distribution. The M_n values determined during the experiments did not show significant deviations in case of different cationizing agents.

III. Tudományos közlemények és konferencia-részvételek / Scientific publications and lectures

III.1. Az értekezés témájához kapcsolódó közlemények / Publications in the field of the dissertation

1. S. Kéki, L. Sz. Szilágyi, J. Török, Gy. Deák, M. Zsuga: High Aggregation Number Silver Clusters by Matrix-Assisted Laser Desorption/Ionization: The Role of Matrices on the Gas-phase Reduction of Silver Ions, *J. Phys. Chem. B.* **107(20)**, 4818 (2003)

2. S. Kéki, L. Sz. Szilágyi, Gy. Deák, M. Zsuga: Identification and Fragmentation Study of Plasticizers with Post-source Decay Matrix-assisted Laser Desorption/Ionization Mass Spectrometry, *Rapid Comm. Mass Spectrom.* **17(8),** 783 (2003)

3. S. Kéki, L. Sz. Szilágyi, Gy. Deák, M. Zsuga: Effect of Different Alkali Metal Ions on the Cationization of Polyethylene Glycols in Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry: A New Selectivity Parameter, *J. Mass Spectrom.* **37***,* 1074 (2002)

4. Sándor Kéki, László Sz. Szilágyi, János Török, György Deák, Miklós Zsuga: A MALDI-TOF MS alkalmazása a kémiai szerkezet-felderítésben, *Studia Universitatis "Vasile Goldis", Arad, Seria B,* **3**, 11 (2001)

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III.2. Egyéb közlemények / Other publications

1. J. Yun, R. Faust, L. Sz. Szilágyi, S. Kéki, M. Zsuga: Effect of Architecture on the Micellar Properties of Amphiphilic Block Copolymers: Comparison of AB Linear Diblock, A_2B_2, A_3B_3 and $(AB)_3$ Star-Block Copolymers, *J. Macromol. Sci.* **A41(6),** 613 (2004)

2. J. Yun, R. Faust, L. Sz. Szilágyi, S. Kéki, M. Zsuga: Effect of Architecture on the Micellar Properties of Amphiphilic Block Copolymers: Comparison of AB Linear Diblock, A^1A^2B and A_2B Heteroarm Star Block Copolymers, *Macromolecules,* **36(5),** 1717 (2003)

3. J. Yun, R. Faust, L. Sz. Szilágyi, S. Kéki, M. Zsuga: Investigation of Architecture Effect on the Micellization of Hetero Three Arm A^1A^2B Star Block Copolymers: Poly(IB_1-star-IB_2-star-MeVE), P*olym. Prep.* **43,** 362 (2002)

4. Szilágyi Sz. L., Kéki S., Deák Gy., Zsuga M.: Poli(izobutilén)-poli(sztirol) diblokk kopolimerekből képződött micellák vizsgálata fényszórás fotometriával, *Műanyag és Gumi*, **363**, 10 (2000)

IF(összes):4,30

III. 3. Az értekezés témájához kapcsolódó konferencia-részvételek / Lectures in the field of the dissertation

1. Szilágyi Sz. László, Kéki Sándor, Török János, Deák György, Zsuga Miklós: Ezüst-klaszterek előállítása MALDI körülmények között. *Nemzetközi Vegyészkonferencia,* Arad, Románia (2003)
   (előadás)

2. Szilágyi Sz. László: Szintetikus polimerek gőzfázisú kationizációja MALDI körülmények között. MTA Műanyag Munkabizottsági Ülés, Budapest 2003. április 28.
   (előadás)

3. Szilágyi Sz. László, Kéki Sándor, Deák György, Zsuga Miklós: Ipari lágyítók meghatározása MALDI-TOF MS módszerrel, *VIII. Nemzetközi Vegyészkonferencia*, Kolozsvár, Románia (2002. november 15-17.)
   (előadás)

4. Kéki Sándor, Deák György, Szilágyi Sz. László, Zsuga Miklós: Önszerveződő rendszerek. *VIII. Nemzetközi Vegyészkonferencia,* Kolozsvár, Románia (2002. november 15-17.)
   (előadás)

5. László Sz. Szilágyi, Sándor Kéki, János Török, György Deák, Miklós Zsuga: A MALDI-TOF MS alkalmazása a kémiai szerkezet-felderítésben, *Nemzetközi Vegyészkonferencia,* Arad, Románia (2001)
   (előadás)

III. 4. Egyéb konferencia-részvételek / Other lectures

1. J. Yun, L. Sz. Szilágyi: Investigation of Architecture Effect on the Micellization of Hetero Three Arm A^1A^2B Star Block Copolymers: Poly(IB_1-star-IB_2-star-MeVE), *ACS Meeting*, Boston, MA, USA (2002)
   (előadás)

2. Szilágyi Sz. L.: Poli(izobutilén)-poli(sztirol) diblokk kopolimerekből képződött micellák vizsgálata fényszórás fotometriával, *XXIV. OTDK konferencia*, Technológia „B" szekció, Veszprém (1999)
   (előadás)