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Review

Mass spectrometric imaging of synthetic polymers

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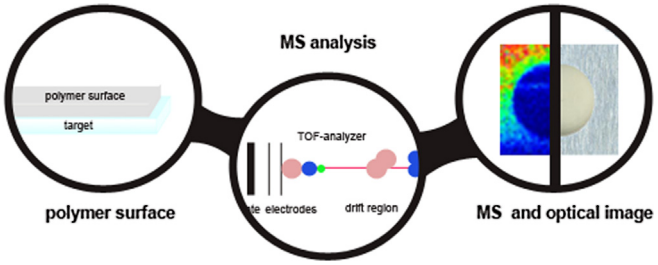
HIGHLIGHTS

- Principals of mass spectrometric imaging (MSI) of synthetic polymers.
- The ionization techniques SIMS and MALDI for MSI are compared.
- A short perspective about polymer blend SIMS-MSI is presented.
- An overview of recent applications and future prospects is given.

GRAPHICAL ABSTRACT



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ABSTRACT

The analysis of synthetic polymers represents today an important part of polymer science to determine their physical properties and to optimize the performance of polymeric materials for block copolymers as well as blend systems. The characterization can easily and rapidly be performed by mass spectrometry. In particular, the film formation of a synthetic polymer is of interest in material research and quality control, which can be determined by employing mass spectrometric imaging (MSI) using secondary ion mass spectrometry (SIMS) or matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. MALDI-MSI has been rapidly improved for the analysis of tissue cross-sections due to its soft ionization and accessible *m*/*z* range, which both also play an important role in polymer science. On the other hand, SIMS-MSI enables a sub-micrometer molecular spatial resolution, which is limited in MALDI-MSI due to the spatial resolution capabilities of the laser desorption process. The aim of the present contribution is to summarize recent advances in both imaging techniques for the analysis of synthetic polymers and to highlight their capabilities to correlate several imaging modalities in future applications.

Contents

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Anna C. Crecelius graduated with a Dipl. Ing. (FH) at the Hochschule Fresenius in 1999 and obtained her Ph.D. at the Sheffield Hallam University in U.K. in 2002. She has conducted post-doctoral research stays at universities including Vanderbilt University (Nashville, TN, USA) and Ludwig Maximillian Universität München. Currently, she is a research fellow at the Friedrich Schiller Universität Jena in the research group of Prof. Ulrich S. Schubert, leading the mass spectrometry activities. Her publication record shows over 35 refereed articles including one book chapter, with an H-index of 14 and over 633 citations.

Jürgen Vitz received his diploma degree in 1999 and obtained his Ph.D. in 2004 under the supervision of Prof. Karsten Krohn at the University of Paderborn. In 2006 he moved to the group of Stéphanie Legoupy at the Université du Maine (Le Mans, France) as a post-doctoral fellow. Thereafter, in 2007, he joined the group of Prof. Ulrich S. Schubert at the Eindhoven University of Technology (TU/e; Netherlands) and, in 2009, he changed to the Friedrich Schiller University Jena (Germany). His research is focused on polymerizations using high-throughput approaches, including organic synthesis, catalysis as well as ionic liquids as alternative reaction media.

Ulrich S. Schubert studied chemistry in Frankfurt and Bayreuth and the Virginia Commonwealth University, Richmond (USA). His Ph.D. studies were performed at the Universities of Bayreuth and South Florida/Tampa (USA). After postdoctoral training with Jean-Marie Lehn at the University in Strasbourg (France), he moved to the TU München and obtained his Habilitation in 1999. From 1999 to 2000 he was Professor at the Center for NanoScience, University of Munich, and from 2000 to 2007 Full-Professor at TU Eindhoven (The Netherlands). Currently he holds a chair at the Friedrich Schiller University Jena with research interest in nanoparticle systems as sensor and drug delivery devices, supramolecular chemistry, inkjet printing of polymers, polymers for energy applications, and self-healing materials.

1. Introduction

Soft ionization mass spectrometry is a powerful characterization technique in polymer science to gain information about the molar masses, polydispersity index values, and end-group structures of synthetic polymers [1,2]. These physical properties are in particular important for tailor-made polymers in high-performance application fields, e.g., health care, life science, car or aviation industries. Besides, the macroscopic as well as microscopic surface-composition of these polymers is of high interest, which can easily be figured out by employing mass spectrometric imaging (MSI). This imaging technique of soft surfaces, including organic, polymeric, and biological material, has been remarkably advanced lately, as indicated by the enormous increase in the number of publications as presented in Fig. 1a. However, MSI analysis of synthetic polymers plays only a very minor role even though the number of publications has been raised recently (see Fig. 1b). Most publications are still concentrated on biomedical tissue applications (for an in depth study of relevant developments in this area the reader is referred to Ref. [3]). The aim of this contribution is to highlight the potentials of MSI in the field of synthetic polymers by explaining its principals, providing an overview of recent applications and future prospects to inspire more researchers to use this emerging technique. Visualizing methods will be one of the exploding characterization tools in analytical chemistry and its combination to gain substantial information will be one of the main approaches.

2. Principals

Mass spectrometric imaging utilizes a probe (primary ions or a laser) to sputter or desorb species directly from the surface, as illustrated in Fig. 2 (step 1).

The generated ions are subsequently separated in a corresponding analyzer and detected. A typical analyzer used in MSI for analyzing synthetic polymers by MALDI and SIMS is a time-of-flight (TOF) analyzer in which the time is recorded that the ions require reaching the detector. To obtain an image of the polymer material, not only one position is analyzed, rather a x,y – pattern is analyzed from which always a mass spectrum is generated as presented in Fig. 2 (step 2). This is typically achieved by a movable stage. The final step in a MSI analysis (see Fig. 2, step 3) is to generate ion images from different mass signals by using certain software packages, which can either be purchased with the mass spectrometer or can be downloaded from a non-commercial source [4].

Mainly the two ionization techniques, namely SIMS [5] and MALDI [6,7] are currently used to investigate synthetic polymer surfaces. The reader is recommended to Ref. [8] by Mahoney for an in-depth coverage of SIMS in the field of polymer science. Both techniques, SIMS and MALDI, are very complementary as outlined in Table 1.

The main advantage of MALDI-MSI is the theoretically unlimited m/z range due to the TOF analyzer and its soft ionization, yielding intact species. However, MALDI-MSI can certainly not compete with the spatial resolution of SIMS-MSI, which can be 100 nm as reported in Ref. [9]. Instead, the highest resolution of MALDI-MSI is up to now in the range of 1–5 μm [10,11]. A more detailed comparison of the benefits and challenges of both imaging techniques is provided in Table 2.

SIMS owns an excellent surface sensitivity, which requires a clean performed sample preparation to avoid any contamination. To achieve higher sensitivities and an increase in the m/z range for SIMS-MSI the surface can be covered with a typical organic MALDI matrix, such as 2,5-dihydroxybenzoic acid (DHB) [12]. In the case of matrix-enhanced ME-SIMS, DHB can be electrosprayed to obtain fine crystals, which enables a spatial resolution of below 3 μm and a reachable m/z range up to 2500 for the imaging experiments. Another possibility to enhance the sensitivity is to evaporate a metal, such as gold, on the polymer surface. With this sample pretreatment, the SIMS-MSI analysis of a poly(styrene) coating with a molar mass above 1000 was possible [13] without the necessity to lower the spatial resolution. Finally, the combination of both approaches, the coating of the surface with an organic MALDI matrix and afterwards with a metal layer, was also tested, enhancing the achievable m/z range without decreasing the spatial resolution [14]. A sub-monolayer coverage of metal nanoparticles strengthened as well the SIMS signals of the analyzed polymer films [15].

The sample preparation required for MALDI-MSI is very crucial for imaging polymer surfaces, as the homogeneity of the matrix–polymer mixture greatly influences the quality of the recorded MSI data [16,17]. Even the temperature plays an important role, as presented in Fig. 3 for the dried-droplet preparation of PEG 1000. At elevated temperatures the polymer is higher concentrated at the outer rims of the shown droplets (A, B, and C).