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Analysis method

Structural and end-group analysis of synthetic acrylate co-polymers by matrix-assisted laser desorption time-of-flight mass spectrometry: Distribution of pendant carboxyl groups

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ABSTRACT

A generally accepted strategy in the development of polymers for interaction with biological systems is control of chemically active functional groups and their concentration within polymer chains. From that perspective, there is a strong need for careful study of polymer structure and distribution of pendant functional groups within macromolecules. One of the materials of particular interest is polymethyl methacrylate-co-methacrylic acid (PMMA-co-MAA). We have performed a detailed matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-ToF-MS) characterization of PMMA-co-MAA (synthesized with different monomer ratios) in order to establish the molecular mass distribution, polymer end groups and exact molecular structures present in the polymer systems. Experimental results have confirmed the successful formation of the materials, based on pre-determined theoretical compositions, with close control over macromolecular structure. Furthermore, a detailed structural analysis of each composition has provided valuable information about the variation of concentration of carboxyl functional groups, generated from MAA co-polymer segments.

1. Introduction

Over the past two decades, mass spectrometry (MS) analysis of polymeric materials has been highly influenced by matrix-assisted laser desorption time-of-flight MS (MALDI-ToF-MS) [1]. Synthetic polymers are thermally unstable, fragile and fragment when ionized by conventional methods, which has limited the use of MS as a means of characterization [2]. MALDI-ToF-MS have minimized these problems by using a soft ionization technique which allows mass determination of molecules by ionization and vaporization without fragmentation. Various studies in the field of molecular MS have shown that, for a wide range of polymers of limited polydispersity (PD< 1.2), MALDI-ToF-MS can provide reasonably accurate average molecular mass information [2]. MALDI-ToF-MS has the potential to provide, not only the molecular mass and mass distribution for synthesized polymers, but also makes possible a detailed and accurate end group analysis and, in particular cases, branching information of the compounds [3]. Taking advantages of a single fast analysis, MALDI-ToF-MS structural information can readily be established, which is important for determination of absolute polymer structures [1].

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For each successful MALDI-ToF-MS experiment, selection of appropriate matrix, solvent and ionizing agent are of a great importance. Structural analysis can be particularly crucial in the case of synthetic polymers as they vary in their polarity, solubility and behavior toward counter ions [2]. Sample preparation has also played a vital role in accuracy of the results. The final aim for matrix, ionizing agent and solvent in sample preparation is to co-crystallize the matrix and polymer in the most homogeneous way. In MALDI-ToF-MS analysis of synthetic polymers, sample preparation typically results in inhomogeneous crystallization so the "laser spots", which give the best possible spectral resolution, have to be found manually during the experiment [4]. The other important parameter in successful MALDI-ToF-MS analysis is the spotting technique. Many different methods have been developed so far, such as dried-droplet method (the oldest reported method) [5], fast crystallization technique (by using vacuum chamber) [6–8] electro-spray deposition (for extra homogeneous spot) [9,10] and spin coated layers which has resulted in more homogeneous surfaces and subsequent higher sensitivity [11,12].

Among the family of synthetic polymers, polyacrylate materials have drawn a great deal of interest in the biomedical field. Those unique polymeric materials have demonstrated excellent performance in, for example, production of biomaterials for diagnostic imaging and fabrication of biosensor devices due to their properties such as low specific weight, high impact resistance and flexibility [13]. The general concept of using polymeric platforms in such applications relies, to a large extent, on the carful design of the polymer structure that would interface with sensitive and highly selective biological systems [13]. For that reason, better understanding of macromolecular composition, structure, block co-polymers and end group determination of the compounds seems to be of crucial importance. In this paper, we report the synthesis and MALDI-ToF-MS characterization of polymethyl methacrylate-co-methacrylic acid (PMMA-co-MAA) polymers in different molar ratios of the monomers, methyl methacrylate/methacrylic acid (MMA/MAA), which have been prepared via well-established free-radical polymerization technique. Molecular mass determination and structural analysis of the synthesized co-polymers were performed with MALDI-TOF-MS (by using layer-by-layer spotting technique). We report a detailed end group and co-polymer analysis that provides essential information, necessary for future application and design of polyacrylate systems in biomedical research.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), methacrylic acid (MAA), 2, 5-dihydroxy benzoic acid (DHB), sodium iodide (NaI), and ethanol (EtOH) were purchased from Sigma Malaysia. Tetrahydrofuran (THF, Thermo Fisher Scientific, US) was used as solvent in polymer synthesis and processing procedures. The free-radical initiator azobisisobutyronitrile (AIBN) was purchased from Friedemann Schmidt Chemical, Germany. MMA monomer was purified by distillation before free-radical polymerization. All other materials have been used as received.

2.2. Synthesis and processing of PMMA-co-MAA

Four different compositions of the PMMA-co-MAA were synthesized by free-radical polymerization using THF as solvent and AIBN as initiator, as reported previously [14]. In brief, MMA and MAA monomers were used in reaction mixtures with variation in initial concentrations as follows: pure PMMA, PMMA-co-MAA (9:1), PMMA-co-MAA (7:3) and PMMA-co-MAA (5:5); the numbers in brackets represent the molar ratios of MMA/MAA. A two-neck round-bottom flask was charged with 50 ml of THF and pre-calculated volume of MMA. A mixture of MAA and initiator (AIBN. 0.328 g) was added to the solution and the polymerization reaction was carried out for 6 hours at 90°C. The reaction was stopped by pouring the reaction solution into distilled water. The polymer precipitate was filtered and washed thoroughly with water, freeze-dried and stored in a refrigerator for further experiments.

2.3. Sample preparation and MALDI-ToF-MS analysis

NaI was used as ionizing agent (100 mg of NaI in 1 ml of EtOH), and matrix solution was prepared by dissolving 100 mg of DHB in 1 ml of EtOH. In order to prepare polymer solution, 10 mg of raw polymer was dissolved in 1 ml of THF. Layer by layer deposition was chosen as the spotting method. 0.5 μl of DHB solution was deposited (first layer) and dried on the sample plate. A layer of NaI solution (0.5 μl) was added on top of the dried matrix as second layer. After another drying step, the subsequent layer of the polymer solution was deposited on the top of the crystallized NaI-DHB mixture (0.5 μl) [15]. It is recommended to use only one solvent for dissolving ionizing agent (salt), matrix and polymer for sample preparation. This may reduce the risk of segregation, as even a relatively small concentration of polymer non-solvent might result in error in obtained data. However, salts are barely soluble in organic solvents which can dissolve synthetic polymers [4]. For that reason, searching for the "sweet" spots for analysis was needed [15]. The sample plate was placed in the MALDI-ToF-MS (ABI 4800 plus) analyzer equipped with a nitrogen laser emitting at 375 nm and data acquisition was set to perform in positive ion mode. DATA Explorer software was used for data processing. The acceleration voltage was set to 10 kV in reflector MS mode. All MALDI-ToF mass spectra were collected by averaging the signals of at least 500 individual laser shots.

3. Results and discussion

One of the major advantages of MALDI-ToF-MS over other techniques is the soft ionization in which cations efficiently "wrap the polymers around themselves" [4]. Essentially, this method prevents fragmentation and preserves the structure of the polymer chains, thus allowing us to "see" whole molecules in the mass spectra. Species present after ionization can include a neutral molecule [M]