Analytica Chimica Acta 808 (2014) 115–123

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Influence of fluorination on the characterization of fluorotelomer-based acrylate polymers by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

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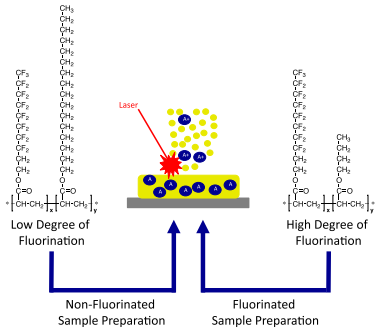
HIGHLIGHTS

- We synthesized six fluorotelomer-based acrylate polymers (FTACPs) having varying degrees of fluorination.
- We explored the sample preparation of FTACPs for MALDI-ToF analysis.
- Increasing the relative degree of FTACP fluorination reduced its compatibility with conventional sample preparation protocols.
- Fluorinated sample preparations improved MALDI-ToF analysis for highly fluorinated FTACPs.
- Characterization of FTACPs was achieved with applicable sample preparation protocols.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form 12 July 2013
Accepted 17 July 2013
Available online 26 July 2013

Keywords:
Fluorotelomer-based acrylate polymer
MALDI-ToF mass spectrometry
Sample preparation
Fluorophilicity

ABSTRACT

The relative degree of fluorotelomer-based acrylate polymers (FTACPs) fluorination was demonstrated to influence the sample preparation protocol for matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrometry. A homologous series of FTACPs were synthesized from fluorotelomer and hydrocarbon acrylates of different chain lengths, which varied the ratio of perfluorinated to hydrogenated carbons (R_F/R_H). The solubility of FTACPs in tetrahydrofuran (THF) and chloroform was observed to decrease for highly fluorinated FTACPs ($R_F/R_H > 0.5$) promoting FTACP aggregation. No dependence on the degree of fluorination was observed for the solubility of FTACPs in the fluorinated solvents α,α,α-trifluorotoluene (TFT) or dichloropentafluoropropanes (HCFC-225). For FTACPs with a low degree of fluorination such as poly(8:2 FTAC-*co*-HDA) ($R_F/R_H = 0.375$), MALDI-ToF analysis was successful using a conventional sample preparation protocol with THF, and dithranol (Dith) matrix. Conversely, the poor solubility of the highly fluorinated poly(8:2 FTAC-*co*-BA) ($R_F/R_H = 1.5$) in THF resulted in mass discrimination. Several fluorinated sample preparation protocols were evaluated for poly(8:2 FTAC-*co*-BA) using TFT and HCFC-225, and decafluoroazobenzene (DFAB) or 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) matrices. The high volatility of HCFC-225 decreased FTACP pooling

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0003-2670/$ – see front matter
http://dx.doi.org/10.1016/j.aca.2013.07.039

during solvent evaporation in comparison to the less volatile TFT, and improved the quantity of detectable signals. MALDI-ToF analysis of poly(8:2 FTAC-*co*-BA) in a 95:5 HCFC-225:methanol with DCTB being the best sample preparation protocol for highly fluorinated FTACPs in this study producing the highest number of observable signals. Employing a fluorinated sample preparation offers the capability of analyzing other highly fluorinated polymers that are not compatible with conventional sample preparations.

1. Introduction

Fluorotelomer-based acrylate polymers (FTACPs) are a group of fluorinated polymers belonging to the class of side-chain fluorinated polymer that also includes urethane and oxetane materials [1]. Like all fluorinated polymers, the attractiveness of FTACPs stems from the improved repellency, lubricity, and chemical and thermal stability when the hydrogen atoms are replaced by fluorine atoms [2]. However, unlike other classes of fluorinated polymers such as fluoropolymers (i.e. polytetrafluoroethylene (PTFE)) and perfluoropolyethers (PFPEs), FTACPs do not possess a fluorinated backbone, but rather fluorinated appendages covalently bound by an ester moiety to a hydrocarbon backbone. When applied to a material, the fluorinated appendages are thought to orientate perpendicular to the surface, which optimizes the number of surface-CF_3 units and reduces the critical surface energy [2,3]. This reduction in critical surface energy makes FTACPs highly effective surface protectants in the carpet, textile, upholstery and paper industries [4].

The term "fluorotelomer-based" denotes the incorporation of material derived from the telomerization process developed by the Du Pont Company in the early 1940s [5–7]. For FTACPs, this refers to the polymerization of fluorotelomer acrylates [CH_2=CHC(O)$OCH_2CH_2(CF_2)_nCF_3$, n = 1–17]. The preparation of FTACPs is often carried out by free radical polymerization in an aqueous emulsion using a combination of fluorotelomer and hydrocarbon acrylates, and often other non-fluorinated monomers [8,9]. By varying the ratio and chain length of the fluorotelomer and hydrocarbon acrylates the wettability and tackiness can be optimized for a specific function [10–12]. Generally, the desirable hydrophobic and oleophobic properties are achieved when the fluorotelomer acrylate has ≥8 perfluorinated carbons and the hydrocarbon acrylate has ≥10 hydrogenated carbons [10,13,14]. Additional non-fluorinated monomers, such as hydroxyl acrylates, are often employed as minor constituents to improve the solubility [15–21], offer cross-linking capability [15–18], and facilitate stain and dirt removal during laundering [15–21]. The diversity of monomer composition has led to FTACPs becoming the largest fraction of commercial fluorotelomer products [4,22], constituting >80% of all fluorotelomer-based raw materials produced worldwide [23].

The high degree of fluorination and copolymerization of multiple monomers poses several challenges for the characterization of FTACPs. Techniques such as near-edge X-ray absorption fine structure (NEXAPS) [24–27]. X-ray photoelectron spectroscopy (XPS) [24,28,29], angle-resolved XPS (ARXPS) [24,30], and scanning electron and force microscopy (SEM and SFM) [19,24], provide information regarding the surface morphology of side-chain fluorinated polymers including FTACPs, but lack molecular weight information. The estimation of weight average and number average molecular weight (M_w and M_n) are traditionally carried out by gel permeation chromatography (GPC). However, M_w and M_n can be misrepresented for FTACPs due to their poor solubility in conventional GPC solvents such as chloroform and tetrahydrofuran (THF) [19]. GPC analyses using fluorinated solvents such as hydrochlorofluorocarbons (HCFCs) [31–33] or α,α,α-trifluorotoluene (TFT) [34–36] have been reported to overcome solubility issues associated with highly fluorinated side-chain polymers. Although this approach can offer a better estimation of molecular weight, it does not provide structural information such as end-groups and monomer distribution.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrometry has evolved into an integral technique for synthetic polymer characterization, which provides both molecular weight properties and structural information [37–40]. Establishing an appropriate sample preparation protocol largely dictates the success of the MALDI-ToF analysis, and can be influenced by the solubility of the target polymer [41,42]. FTACPs provide a unique challenge as their relative degree of fluorination can render conventional sample preparations ineffective. Presently, a handful of studies have explored the MALDI-ToF analysis of side-chain fluorinated polymers, however none were fluorotelomer-based [43–46]. In these studies, polymers having a relatively low degree of fluorination were soluble in non-fluorinated solvents and were successfully analyzed using the MALDI matrices 2,5-dihydroxybenzoic acid (DHB) [44] and dithranol (Dith) [45,46]. On the other hand, polymers having a higher degree of fluorination were insoluble in THF, and required a multi-layer sample preparation where the polymers were prepared in the now banned trichlorotrifluoroethane (CFC-113) [43]. It is generally accepted that single-solvent systems are the preferred sample preparation protocols as they reduce the likelihood of sample segregation that can occur with multi-solvent systems [47,48].

Our interest in establishing a sample preparation protocol for the MALDI-ToF analysis of FTACPs stems from their potential to serve as sources of perfluorinated carboxylates (PFCAs) [49,50]. PFCAs are persistent environmental contaminants that have been demonstrated to accumulate in biota with increasing perfluorinated chain length (>6 CF_2) [51,52]. Although FTACPs have not yet been confirmed as a PFCA source, other fluorotelomer-based commercial products, such as polyfluoroalkyl phosphate esters (PAPs) [53] and fluorotelomer stearate monoester (FTS) [54,55], are known to biodegrade to PFCAs. In the present work, we investigated the influence of FTACP fluorination on the MALDI-ToF sample preparation to facilitate a future biodegradation study of FTACPs. A homologous series of FTACPs were synthesized for this study. Scanning electron microscopy (SEM) was used to supplement the MADLI-ToF results by providing a surface distribution image for the various sample preparation protocols.

2. Experimental

2.1. Chemicals

2,2-Azobis(2-methylpropionamide) dihydrochloride (AIBA, 98%), 2,3,4,5,6-pentafluoroaniline (99%), 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, ≥98%), acetone-d_6 (99.9%), butyl acrylate (BA, ≥99%), dithranol (Dith, 98.5%), sodium trifluoroacetate (NaTFA, 98%), sodium hypochlorite, *tert*-butyl methyl ether (MTBE, ≥99%), tetrabutylammonium hydrogen sulfate (n-Bu_4NHSO_4, 97%), tetrahydrofuran (THF, ≥99%) and α,α,α-trifluorotoluene (TFT, ≥99%) were all purchased from Sigma Aldrich (St. Louis, MO). Chloroform (≥99.9%) and ethyl acetate (≥99.9%) were purchased from Fisher Scientific