Contents lists available at ScienceDirect

Journal of Chromatography A

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

Acid monomer analysis in waterborne polymer systems by targeted labeling of carboxylic acid functionality, followed by pyrolysis – gas chromatography



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ARTICLE INFO

Article history: Received 23 February 2018 Received in revised form 7 May 2018 Accepted 12 May 2018 Available online 14 May 2018

Keywords: Pyrolysis-GC Derivatization (Meth)acrylic polymers

ABSTRACT

Pyrolysis – gas chromatography – (PyGC) is a common method to analyse the composition of natural and synthetic resins. The analysis of acid functionality in, for example, waterborne polyacrylates and polyurethanes polymers has proven to be difficult due to solubility issues, inter- and intramolecular interaction effects, lack of detectability in chromatographic analysis, and lack of thermal stability. Conventional analytical techniques, such as PyGC, cannot be used for the direct detection and identification of acidic monomers, due to thermal rearrangements that take place during pyrolysis. To circumvent this, the carboxylic acid groups are protected prior to thermal treatment by reaction with 2-bromoacetophenone. Reaction conditions are investigated and optimised *wrt*. conversion measurements. The aproach is applied to waterborne polyacrylates and the results are discussed. This approach enables identification and (semi)quantitative analysis of different acid functionalities in waterborne polymers by PyGC.

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1. Introduction

The variety of applications of waterborne polymeric dispersions is broad and ranges from uses in paints, adhesives, paper coatings, floor polishes, printing inks and textile finishes to pharmaceuticals, including sustained- and controlled-release formulations. The application range for these waterborne polymers will continue to expand, due to stricter requirements for emissions of organic compounds, such as used in traditional solvent-borne coating systems.

The variation in the chemical composition of synthetic resins can be very large, with combinations of monomers tailored to specific application needs. Most often resins are prepared using functional monomers, such as hydroxy-, ketone- and carboxylic-acid-functional groups. These monomers allow specific applications, such as cross-linking in two-component systems or stabilization of polymer particles in aqueous environments.

In waterborne polyacrylate dispersions, the two most common acidic compounds that are incorporated in the acrylic polymer backbone are acrylic acid (AA) and methacrylic acid (MAA), while waterborne polyurethane dispersions are created using dimethylolpropanoic acid (DMPA) monomer.

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https://doi.org/10.1016/j.chroma.2018.05.024 0021-9673/© 2018 Elsevier B.V. All rights reserved. To determine the overall chemical polymer composition, several approaches can be used. Nuclear-magnetic-resonance (NMR) spectroscopy and Fourier-transform infrared (FTIR) spectroscopy are frequently used to obtain an average composition of the polymer. FTIR is not applicable to detect acid content in polymers, because the sensitivity is limited and because the technique cannot discern between acrylic and methacrylic acids. NMR may in principle be used, but it is a complex technique that requires significant expertise to obtain the required information.

Besides NMR and FT-IR, a common way to determine the average chemical composition is pyrolysis gas chromatography (PyGC). With this technique the polymer is heated to elevated temperatures (500–1400 °C) in the presence of an inert gas, which results in thermal decomposition of the polymer chains [1–5]. Performing pyrolysis on polymers results in the formation of reproducible decomposition products, which are characteristic for the original (co)polymer composition. The volatile fraction of these decomposition products are chromatographically separated by gas chromatography (GC) and detected by mass spectrometry (MS) and/or flame-ionization detection (FID). PyGC-FID/MS analysis of polyacrylates allows determination of the original starting monomeric units as decomposition products. Especially, non-functional (meth) acrylic ester groups show reproducible thermal decomposition to their original monomeric structures [3], such as methyl-methacrylate (MMA), methyl acrylate (MA), butyl



methacrylate (BMA), butyl acrylate (BA), 2-ethyl hexylacrylate (2-EHA) and 2-ethyl hexylmethacrylate (2-EHMA).

In general, due to inter- and intramolecular thermal rearrangements, the polymer composition has an influence on the nature of the observed thermal decomposition products. Specifically, in the case of (meth)acrylic esters it is known that side products (alcohol and alkene degradation products) are formed during pyrolysis (Fig. 1). The resulting volatile products of the pyrolysis of (meth)acrylic esters can be identified and quantified with reasonable accuracy, due to the high precision of the analysis.

However, in PyGC analysis of polyacrylates containing acidfunctional acrylic monomers, the accuracy (recovery) and precision (repeatability) of the acid-functional monomers are often not satisfactory [6]. Moreover, it is not possible to distinguish between the presence of incorporated acrylic- or methacrylic acid in acrylic copolymers, because thermal decomposition of other (meth)acrylic monomer esters (such as BA or BMA) results in the formation of (meth)acrylic acid [5]. The selectivity of direct pyrolysis of (meth)acrylates is, therefore, limited.

At pyrolysis temperatures, acrylic acid monomers segments may rearrange to anhydrides with the loss of water (Fig. 1). The anhydrides formed are thermally unstable, undergoing decarboxylation and subsequent reactions [6]. The resulting compounds are commonly non-volatile and cannot easily be related to the starting (meth)acrylic monomer.

Direct analysis of acid functionality with PyGC is, therefore, generally problematic to perform. Even if the incorporated (meth)acrylic acid is thermally decomposed to the intact monomer, difficulties will be encountered with both separation and detection. Common GC columns used in PyGC are not suitable for the analysis of carboxylic acids, as broad and asymmetrical peaks are typically observed. Due to the relatively low amount of carbon present in (meth)acrylic acid compared to other (meth)acrylic monomers, there is also a relatively low sensitivity in FID detection. The poor separation and detection of the (meth)acrylic acid monomers can be negated using pyrolysis-liquid chromatography (PyLC) as described by Van der Horst et al. [7]. Collecting the (meth)acrylate pyrolysate in a cryogenic trap enables analysis with liquid chromatography (LC) combined with photodiode-array detection (PDA). The main advantage of using this type of setup is that detection is based on the molar response of the C=C carbon unsaturations in (meth)acrylic monomers. Another approach to improve the separation and detection of acrylic acids, has been described by Osete-Cortina et al. [8] and Van der Peyl et al. [9]. They show that the (meth)acrylic-acid degradation products from (meth)acrylic-ester monomers in pyrolysis can be reacted with a trimethylsilyl reagent to obtain better peak shapes for (meth)acrylic acid. Due to the fact that (meth)acrylic acid can also be present as a degradation product of (meth)acrylic esters, the direct pyrolysis in the presence of silylation reagents (or any other derivatization reagent used) is not representative for the acid type or total concentration of incorporated acid.

Both approaches described [7–9], focus on improvement of the separation and detection of (meth)acrylic pyrolysates using direct pyrolysis of the sample, while the main problem in the pyrolytic characterization of (meth)acrylic resins is the formation of rearrangement products during the pyrolysises. A double-shot pyrolysis method, in which the reagent and solvent are evaporated first, followed by a pyrolysis step of the derivatized polymer residue deposited in the liner, yields a better representation of the type and amount of acid present, since no side reaction of pyrolytically degraded (meth)acrylic acid with derivatization reagent can occur.

Apart from trimethylsilylation using reagents such as BSTFA (*N*,*O*-*bis*(trimethylsilyl)acetamide) or MSTFA (*N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide), other common derivatization reagents used in the small molecule analysis of carboxylic acids are chloroformates [10,11] and bromo-acetophenone compounds [12,13].

Derivatization of polymers prior to analysis may be a useful tool to obtain information which is not readily obtainable in another way, such as the incorporation of acid functionalities in acrylic polymers. Specifically, applying derivatization of specific functional groups in combination with chromatography and selective detection techniques, such as ultraviolet (UV) or fluorescence spectroscopy or MS, may yield valuable information on molecular architecture. The challenges for the derivatization of polymers



 $(R = -H \text{ or } -CH_3, R' = CH_3, (CH_2)_nCH_3)$

Fig. 1. Schematic pyrolysis reaction pathway for a copolymer of (meth)acrylic acid and alkyl (meth)acrylate. Alkene release was exemplified using R'=(CH₂)₃CH₃.

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