



Selective separation of fluorinated compounds from complex organic mixtures by pyrolysis-comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry



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ABSTRACT

The usefulness of comprehensive two-dimensional gas chromatography (GC × GC) was demonstrated for the selective separation of fluorinated compounds from organic mixtures, such as kerosene/perfluorokerosene mixtures, pyrolysis products derived from polyethylene/ethylene-tetrafluoroethylene alternating copolymer mixture and poly[2-(perfluorohexyl)ethyl acrylate]. Perfluorocarbons were completely separated from hydrocarbons in the two-dimensional chromatogram. Fluorohydrocarbons in the pyrolysis products of polyethylene/ethylene-tetrafluoroethylene alternating copolymer mixture were selectively isolated from their hydrocarbon counterparts and regularly arranged according to their chain length and fluorine content in the two-dimensional chromatogram. A reliable structural analysis of the fluorohydrocarbons was achieved by combining effective GC × GC positional information with accurate mass spectral data obtained by high-resolution time-of-flight mass spectrometry (HRTOF-MS). 2-(Perfluorohexyl)ethyl acrylate monomer, dimer, and trimer as well as 2-(perfluorohexyl)ethyl alcohol in poly[2-(perfluorohexyl)ethyl acrylate] pyrolysis products were detected in the bottommost part of the two-dimensional chromatogram with separation from hydrocarbons possessing terminal structure information about the polymer, such as α -methylstyrene. Pyrolysis-GC × GC/HRTOF-MS appeared particularly suitable for the characterization of fluorinated polymer microstructures, such as monomer sequences and terminal groups.

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1. Introduction

In recent years, fluorinated compounds have rapidly emerged as attractive substances for many fields, such as coatings, lubricants, films, electric materials, optical materials, refrigerants, food containers, analytical reagents, medical devices, and pharmaceuticals [1–5]. A variety of these compounds have widely spread throughout the environment, including in wildlife and humans [6–9]. Their selective separation from highly complex organic mixtures, such as biological tissues, environmental samples, and polymer pyrolysis products, is crucial to understanding their pharmacokinetics, environmental fate, and structure–property relationship [6–9]. Although pyrolysis (Py)-gas chromatography (GC)/mass

spectrometry (MS) is often used to structurally characterize polymers, including fluorinated polymers [10–12], the pyrolysis of fluorinated polymers often generates highly complex organic mixtures that cannot be completely resolved by conventional one-dimensional (1D) GC [11,13].

Over the past decades, comprehensive two-dimensional gas chromatography (GC × GC) has been developed and applied to separate highly complex organic mixtures, such as petroleum, geochemical, and environmental samples [14–18]. Its separation ability is several tens of times higher than 1D GC. In addition to an enhanced separation, it facilitates analyte identification because organic compounds are detected in an orderly fashion according to their volatility and polarity in the two-dimensional (2D) chromatogram. Furthermore, its coupling with high-resolution time-of-flight mass spectrometry (HRTOF-MS) has proven a very powerful analytical approach for complex organic mixtures [14,16,19]. Few reports have addressed GC × GC analyses of fluorinated compounds. Korytár et al. have reported that mono- and di-fluorinated brominated diphenyl ethers (BDEs) can be separated

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from their non-fluorinated counterparts in the 2D chromatogram [20]. A few synthetic polymer analyses have been attempted by pyrolysis-comprehensive two-dimensional gas chromatography (Py-GC \times GC). Eckerle et al. have characterized the short-chain branch structure in polyethylene (PE) by Py-GC \times GC [21]. However, this technique has not been utilized for the structural characterization of fluorinated polymers to date. This study demonstrates the usefulness of GC \times GC/HRTOF-MS for the selective separation of fluorinated compounds from organic mixtures, such as kerosene/perfluorokerosene mixture, pyrolysis products originating from PE/ethylene (E)-tetrafluoroethylene (TFE) alternating copolymer mixture, and poly[2-(perfluorohexyl)ethyl acrylate].

2. Material and methods

2.1. Materials

Kerosene, perfluorokerosene, and PE (HI-ZEX MILLION[®] 145 M) were purchased from Wako Pure Chemical Industries (Osaka, Japan), Tokyo Kasei Kogyo (Tokyo, Japan), and Mitsui Chemical (Tokyo, Japan), respectively. The ethylene (E)-tetrafluoroethylene (TFE) alternating copolymer (E/TFE molar ratio = 46/54) was polymerized from the corresponding monomers in a 3,3-dichloro-1,1,1,2,2-pentafluoropropane/1,3-dichloro-1,1,2,2,3-pentafluoropropane mixture (AK-225[®], Asahi Glass). Poly[2-(perfluorohexyl)ethyl acrylate] was polymerized from the corresponding monomer using N,N'-azobis(isobutyronitrile) as an initiator and cumyl dithiobenzoate as a chain transfer agent in AK-225[®].

2.2. Methods

The Py-GC \times GC/HRTOF-MS system comprised a pyrolyzer (PY-2020iD, Frontier Lab Corporation, Koriyama, Fukushima, Japan) and a Zoex KT2006 GC \times GC jet modulator (Zoex Corporation, Houston, TX, USA) installed on an Agilent 7890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) connected to a JEOL AccuTOF HRTOF-MS instrument (JEOL Corporation, Tokyo, Japan). A pyrolysis sample cup containing about 0.1 mg of sample material was dropped into the pyrolyzer microfurnace. The pyrolysis temperature was set at 600 °C for the polymer analysis and 260 °C for the kerosene/perfluorokerosene mixture analysis. The pyrolyzer-GC interface and the GC inlet were kept at 270 and 260 °C, respectively. The GC oven was held at 40 °C for 5 min before heating to 260 °C at a rate of 3 °C min⁻¹. The separation was performed on the column set of a DB-1MS fused silica capillary column (30 m \times 0.25 mm i.d., 0.25 μ m film thickness, Agilent Technologies) as the first column and a DB-17 fused silica capillary column (2 m \times 0.10 mm i.d., 0.10 μ m film thickness, Agilent Technologies) as the second column. Helium used as a carrier gas for the GC apparatus was supplied at a rate of 1.50 mL min⁻¹. The modulation period was set to 4 s. The modulator hot gas was maintained at 200 °C for 5 min before heating to 350 °C at a rate of 3 °C min⁻¹. The hot gas duration time was 250 ms. The HRTOF-MS was operated at a multi-channel plate voltage of 1900 V and a constant resolving power of approximately 5000 FWHM over a mass range of m/z 45–800 using electron impact ionization (electron-accelerating voltage: 70 V). The data were acquired at 25 Hz. Perfluorokerosene was introduced into the HRTOF-MS ion source during the initial seconds of an analytical run for the m/z calibration. A raw data analysis was conducted using the MassCenter software (JEOL). Contour plots (2D chromatogram) were analyzed using the GC Image software (Zoex).

Non-fluorinated compounds were identified based on the National Institute of Standards and Technology (NIST) MS library. Fluorinated compounds that were not recorded in the library were

identified based on fragmentation analyses of accurate mass spectra obtained by HRTOF-MS while referring to the known pyrolysis products of ETFE and fluorinated acrylic polymers described in the previous reports [13,22].

3. Results and discussion

3.1. Separation of kerosene/perfluorokerosene mixture

Fig. 1 shows (A) 1D and (B) 2D total ion current (TIC) chromatograms of the kerosene/perfluorokerosene (50/50 wt%) mixture. Abscissa and ordinate axes represent the retention times in the first non-polar column and in the second polar column, respectively. Petroleum derivatives, such as kerosene, have been extensively studied by GC \times GC [17,23,24]. Kerosene components were spread over the upper part of the 2D chromatogram and consisted of highly ordered structures based on their physico-chemical properties. These components were eluted according to their boiling point in the first dimension and in terms of their polarity, which was categorized into four chemical groups, i.e., alkanes, naphthenes, mono-aromatics, and di-aromatics, in the second dimension. Alkanes generally appear at the shortest retention times in the second dimension for natural organic compounds, such as hydrocarbons and biologically derived compounds. Therefore, the region below the alkanes in the second dimension is often called “the dead band” and does not show any peaks. Interestingly, fully fluorinated kerosene, or perfluorokerosene, was eluted in the dead band and was completely separated from its hydrocarbon counterparts (kerosene). Highly fluorinated organic compounds usually exhibit unique partition, sorption, and chromatographic properties and often generate a so-called fluoruous phase that does not mix with either water or hydrocarbon phases [25–29]. Goss and Bronner have suggested that highly fluorinated compounds show a weaker van der Waals force than their non-fluorinated counterparts, resulting in their unique partition property [29]. Therefore, the weaker van der Waals force may reduce interactions between the highly fluorinated compounds and the GC columns, significantly shortening their retention times as compared to their hydrocarbon counterparts.

3.2. Separation of pyrolysis products of fluorinated polymers

The ETFE alternating copolymer (Fig. 2) is a representative fluorinated polymer exhibiting remarkable thermal stability, chemical durability, electric property, and mechanical strength, making it interesting for various industrial applications, such as chemical equipment materials, wire-coating insulations, and covering sheets for sports dorms [30]. Therefore, a detailed structural characterization is considerably important for ETFE product development and manufacturing. However, such a structural characterization has encountered technical difficulties because of the insolubility of ETFE in any solvent. Py-GC/MS has emerged as a powerful technique for the structural characterization of insoluble polymers, such as fluorinated polymers [11–13].

Here, PE, the hydrocarbon counterpart of ETFE, acted as an analytical reference in a mixture with ETFE. The Py-GC \times GC/HRTOF-MS analysis of the PE/ETFE (50/50 wt%) mixture provides highly structured 2D TIC chromatogram (Fig. 3). Pyrolyzed PE mainly produced *n*-alkanes, *n*-alkenes, and *n*-alkadienes with different numbers of carbon atoms [11,21]. These products were eluted as clusters (Fig. 3(B)). In each cluster, retention times followed the order: *n*-alkane > *n*-alkene > *n*-alkadiene in the first dimension and *n*-alkane < *n*-alkene < *n*-alkadiene in the second dimension.

On the other hand, ETFE pyrolysis products were eluted in the dead band of the 2D chromatogram and separated from those of

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