Comparison of Pyrolysis behavior between Block and Random Copolymer with Py-GC/APGC-QTof MS and multivariate data analysis

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INTRODUCTION

Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) is one of major analytical techniques for chemical structural elucidation of polymers. It is identification of the gas (pyrolysis gas) generated at almost the same time that several 10 micrograms of plastic pieces are fed into the furnace heated to 600°C under inert gas and the overall chemical structure of polymer can be estimated. It is also used for identification polymer additives in plastics, quality control marker (QC-marker) analysis, especially research the cause of yellow discoloration. Recently, polymer synthesis chemists have great interest for the application on QC-marker analysis of functional polymers such as photoresists and color-resists related to semiconductor and display manufacturing. GC/Electron Ionization (EI)-Quadrupole-MS has been often used as Py-GC-MS and the ionization technique. But the total ion chromatogram (TIC) is extremely complex with increasing the monomer dimension number on copolymer, for various pyrolysis gas are formed on pyrolysis process and fragment ions are produced on ionization. TIC can be improved simple with APGC ionization developed as high sensitivity and soft ionization to observe molecular ion without fragmentation. On multivariate analysis of APGC MS data, it is drastically reduced when carry out peak deconvolution. QTof MS combined with APGC ionization source can be obtained MS and MS/MS spectrum of each peak at same time, elemental composition needed on chemical structural elucidation is achieved from exact mass of molecular and fragment ion on their spectrum. On this time, pyrolysis behavior between acrylic acid -styrene block and random copolymer is compared with Py-GC/ APGC-QTof MS and all markers on each copolymer can be extracted by multivariate data analysis.

METHODS

It is shown for analytical system, method and sample in the following Analytical compound Polystyrene-poly (acrylic acid)/Block and Random Copolymer (Polymer Source Inc.) Pyrolyzer (Fig.1) EGA/PY-3030D (Frontier Lab/ Japan) Pyrolysis temperature : 500°C Sample weight: 50ug GC/MS 7890B (Agilent)/ Xevo G2-XS QTof (APGC ion source) [GC method] Rtx-5MS 0.25mmID x 30m x 0.25um Oven : 60°C à 15°C/min à 300°C (3min.hold) Carrier gas : He, 1.2mL/min (Constant flow) [MS method] APGC Positive, Resolution > 40,000 Corona Current : 2.0uA Data acquisition : MS^E Ch.1 Low energy 2.0ev Ch.2 High energy 5.0 - 35eV (Ramping) Mass Range : 50 to 1200Da (0.1sec./ scan) Lock mass : m/z 355.0705 (column bleed)

RESULTS

Each of block and random co-polymer is accurately measured 50ug into metallic sample cap with microgram scale precision balance and analyzed it each 3 times with Py-GC/APGC-HRMS, base peak intensity (BPI) chromatogram are shown on Figure 2.

It could be confirmed that MS^E technique is useful on identification of pyrolysis gas components generated from polymer. MS^E spectrum of a specific peak on chromatogram analyzed polystyrene-poly (acrylic acid) copolymer is shown in Figure 3 and the peak of chemical structure is elucidated. The inspection result with Mass Fragment software is shown in Figure 4.



Figure 2. BPI chromatogram of copolymer with Py-GC/APGC-HRMS



Figure 4. Result of fragment ion matching by Mass Fragment Software









Figure 7. S and Trend plot on block vs. random Copolymer and extraction of random copolymer marker (OPLS-DA model)



Figure 8. Results of chemical structural elucidation on random copolymer marker components

DISCUSSION

As a result of comparative analysis with OPLS-DA model, a styrene monomer bonded to an acrylic acid dimer, an acrylic acid monomer bonded to a styrene dimer and a styrene trimer are characteristically detected as block co-polymer marker. As shown in Figure 9, the probability that monomer binding to a specific monomer is same in molecular structure of block co-polymer is higher than that of the random copolymer.



Figure 9. Mechanism to produce block copolymer marker

Further analysis of the detailed chemical structure, a carbon atom to which a phenyl group is bonded in a styrene monomer and a carbon to which a carboxylic acid in an acrylic acid monomer is bonded, that is, an α -carbon is directly bonded to each other, a fragment structure capable of affirming irregular polymerization is detected as a unique pyrolysis component on random co-polymer. It is considered that the α - to β -carbon are regularly bonded on block co-polymer chemical structure, whereas in random copolymer, there are also sites bonded in an irregular direction such as α - to α carbon and β - to β -carbon beyond steric obstacles (Figure. 10).



Figure 1. Outline of Pyrolyzer "Py-3030D (Frontier Lab)"

Figure 5. S and Trend plot on block vs. random Copolymer and extraction of black copolymer marker (OPLS-DA model)



Figure 6. Results of chemical structural elucidation on block copolymer marker components

With multivariate data analysis software "Progenesis QI", total ion chromatogram measured block and random polystyrene-poly (acrylic acid) copolymer each 3 times is analyzed. Block co-polymer marker components are extracted on S-plot of OPLS-DA model which is a comparative analysis between 2 groups and confirmed on trend plot (Figure 5). Chemical structural elucidations of marker components are determined with MS^E spectrum and above workflow (Figure 6). Random co-polymer marker components are extracted and elucidated chemical structure using same procedure (Figure 7 and 8).

-Sty<mark>-AA-Sty</mark>-Sty-AA</mark>-Sty-AA-AA-Sty-



Figure 10. Mechanism to produce random copolymer marker

CONCLUSION

It is possible to detect molecular related ions with high sensitivity and determine elemental composition by APGC ionization technique is combined to Py-GC/QTof-MS.

Superiority points to Py-GC/EI-Q mass spectrometry are shown below :

- Molecular-related ions and product ions can be simultaneously acquired without vacuum vent and EI /CI source switching
- Simple mass spectrum : Optimum data quality for multivariate analysis.
- High identification ability : Elemental composition from exact mass spectrum
- Acquisition of high sensitivity and highly comprehensive data •