Analysis of Poly(butyl acrylate) by Py-GC/MS, MALDI-MS and Thermal Desorption and Pyrolysis combined with DART-MS

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Introduction

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and matrix-assisted laser desorption/ionization (MALDI)-MS are widely used for polymer characterization.

Recently, thermal desorption and pyrolysis/direct analysis in real time (TDP/DART)-MS is using for polymer analysis[1-3].

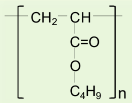
Analytical purposes of polymer products range from raw material's lot survey to failure analysis. Thus, we are aiming at further development of polymer analysis technology, especially for base polymer constituting a polymer products. In this poster, we described our progressing using homopolymer as our first step.

The purpose of this work :

In the view of repeating unit, molecular weight distribution and terminal functional groups, clarifying the characteristics of each analytical methods by measurement data and general theory.

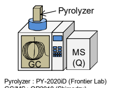
Experimental

◆ Material : Poly(butyl acrylate), PBA (Sigma Aldrich)
*Mw ~99,000 (GPC)



$(C_7H_{12}O_2)_n$
$(128.08)_n$ Da

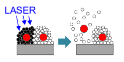
◆ Analytical methods



Pyrolyzer : PY-2020iD (Frontier Lab)
GC/MS : QP2010 (Shimadzu)
6890GC/5975MSD (Agilent)

(a) Py-GC/MS [4]

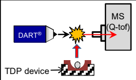
Pyrolyzer: 600 °C
Carrier: He, 100 ml/min
Injection: Split 100 : 1 (1 ml/min at the column), 320°C
Column: Frontier Lab UA-5 (30 m x 0.25 mm id, 0.25 μm)
Oven: 40 °C (2 min) – (20 °C/min) – 320 °C (13 min), Total 29 min
Detector: EI Ionization
Quadrupole, scan range *m/z* 29-600
Sample: ca. 0.2mg



MALDI-TOFMS : autoflex speed (Bruker)

(b) MALDI-MS

Matrix: DCTB
Ionization accelerator: NaTFA
Solvent: THF
Laser: Smartbeam II (355 nm)
Analysis mode: Positive Reflector (accel.19 kV, reflect. 21 kV)
Positive Linear (accel. 19.5 kV)



TDP device : ionRocket (BioChromato)
Ion source : DART®-SVP (IonSense)
MS Spectrometer : compact (Bruker)

(c) TDP/DART-MS

TDP device: RT (1 min) – (100 °C/min) – 600°C, Total 7min
Detector: DART Ionization (Ionization gas: He, 400 °C)
Q-TOF, Mass range *m/z* 50 - 2000
Sample: ca. 0.2mg

Kendrick Mass Defect(KMD) analysis was used a "Spectra Scope (BioChromato)" software.

Results and Discussions

Repeating unit

Py-GC/MS enables identification of polymer type using the available spectral library of pyrolysis products (ex. F-Search, Frontier Lab), (Fig. 1).

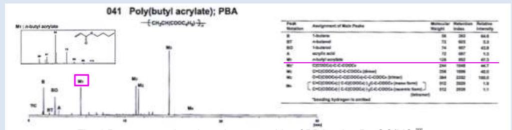


Fig. 1 Pyrogram and peak assignment table of PBA using Py-GC/MS [4]

MALDI-MS enables identification of polymer type using the observed mass interval corresponding to the mass of the repeating unit or the elemental compositions calculated from the mass (Fig. 2).

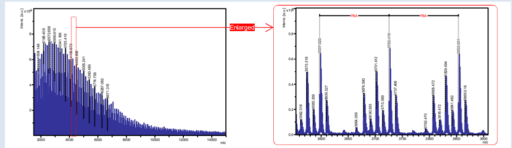


Fig. 2 Mass spectra of PBA using MALDI-MS (reflector mode)

TDP/DART-MS enables identification of polymer type without spectral library using the observed elemental compositions of the repeating unit (Fig. 3).

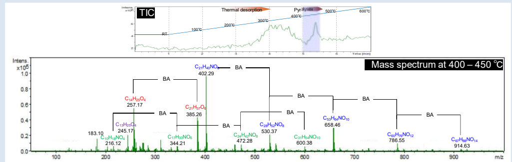


Fig. 3 TIC and Mass spectrum at pyrolysis region of PBA using TDP/DART-MS

Molecular weight distribution

Py-GC/MS disables observation of molecular weight distribution since their analysis target is pyrolysis products.

MALDI-MS enables observation of absolute molecular weight distribution, in case the sample has quite narrow distribution. This PBA has too wide to discuss about average molecular weight (Fig. 4,5). In that case, SEC/MALDI-MS is effective (Fig. 6).

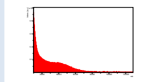


Fig. 4 Mass spectra of PBA using MALDI-MS (liner mode)

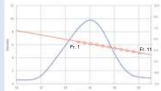


Fig. 5 SEC curve for PBA

Table. Results of SEC/MALDI-MS

	M_n	M_w	M_w/M_n
SEC/MALDI-MS	23,000	165,000	7.17

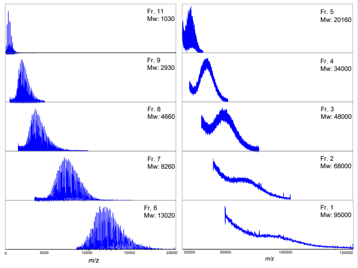


Fig. 6 Mass spectra of PBA using SEC/MALDI-MS

TDP/DART-MS enables measurement of molecular weight distribution of thermal desorption compounds (Fig. 7).

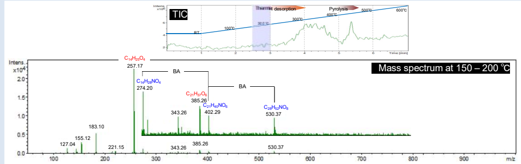


Fig. 7 TIC and Mass spectrum at thermal desorption region of PBA using TDP/DART-MS

Terminal functional groups

Py-GC/MS disables identification of terminal functional groups of unknown polymer samples. But for a known terminal functional groups, quantitative analysis is possible.

MALDI-MS enables analysis how many terminal functional groups. KMD analysis, especially Remainder (R)KM plot[5] is helpful, since the number of terminal functional groups are visualized clearly (Fig. 8).

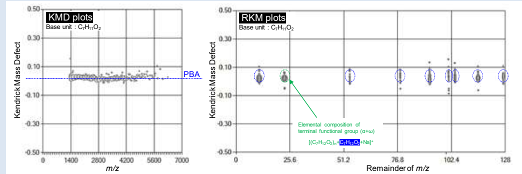


Fig. 8 KMD and RKM plots of PBA using MALDI-MS spectrum (reflector mode, Fig. 2)

TDP/DART-MS enables not only analysis how many terminal functional groups but also elucidation chemical structure of terminal functional groups using accurate mass and MS/MS spectra of thermal desorption products (Fig. 9). KMD and RKM plot[5] are also helpful (Fig. 10).

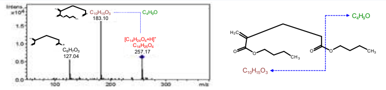


Fig. 9 MS/MS spectrum of *m/z* 257.17 using TDP/DART-MS

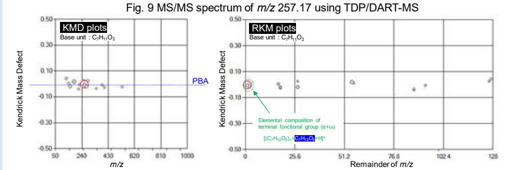


Fig. 10 KMD and RKM plots of PBA using TDP/DART-MS spectrum at thermal desorption region (Fig. 6)

Conclusion

Regarding the measurement samples, Py-GC/MS and TDP/DART-MS enables measurement polymer materials such as vulcanized rubbers and crosslinked resins, but they disables grasp information about molecular weight distribution as-is. On the other hand, MALDI-MS enables measurement absolute molecular weight distribution as-is only if samples were soluble and have narrow distribution (M_w / M_n < 1.1). Additionally it enables analysis compositional characterization of polymers only if the spectra was measured (excluding vulcanized / crosslinked polymer, fluorine polymer and olefin polymer).

TDP/DART-MS enables individual measurement of low molecular weight pyrolysis products and oligomeric thermal desorption products, since it utilize a DART soft ionization technique combined with TDP device. Therefore, it give us valuable clue to elucidate chemical structure of unknown compounds (ex. Polymers which has wide distribution and compounds not listed in spectral library such as reacted and degraded products). Thus, it can contribute to further development of polymer analysis technology.

Our next step, we will clarify the characteristics of these analytical methods using copolymer, crosslinked polymer and degradation products.

References

1. C.Takei, K.Kinoshita, T.Nishiguchi, h.Shimada, K.Maeno, Y.Shida; 63rd ASMS Annual Conference, Poster ThP74 (2015)
2. R.B.Cody, C.Takei, H.Shimada, Y.Shida, A.Kusai; 64th ASMS Annual Conference, Poster MP545(2016)
3. C.Takei, K.Yoshizawa, H.Ohtani; 65th ASMS Annual Conference, Poster WP605(2017)
4. S.Tsuge, H.Ohtani, and C.Watanabe; Pyrolysis-GC/MS Data Book of Synthetic Polymers, Elsevier (2011) p. 92-93
5. H.Sato, S.Nakamura, K.Teramoto, T.Sato; JASMS, 2014, 25(8), 1346-1355

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