Molecular characterization of terminal structures for polycarbonates using a thermal desorption/pyrolysis DART-MS

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Introduction

Polycarbonates (PCs) are an engineering thermoplastic having excellent properties such as impact resistance and optical transparency. Although most PCs are composed of bisphenol A carbonate repeating unit, their terminal structures are specific to their synthesis route (solvent method, melt method, etc). Furthermore, chemical modifications and copolymerization of PCs should be considered. Therefore, molecular characterization of PCs including terminal structure, branch and so on is important for quality control.

Application for easy method of polycarbonate terminal structure.

Materials and Methods

◆ Materials :

Standard samples
- PC1 (p-t-butylphenoxy terminal types, solvent method)
- PC2 (p-t-cumylphenoxy terminal types, melt method)

Industrial samples
- A, B, C, D (unknown terminal structure samples)

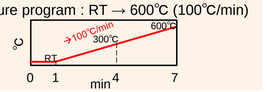
◆ Analytical methods :

Thermal desorption/pyrolysis DART-MS (Fig.1)

0.5 mg of sample were put into the POT. Mass spectra were measured as the samples were heated.

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

Mass Spec. : compact (Bruker)
Ion Source : DART-SVP (IonSense)
Ionization gas : Helium
Helium gas temperature : 400℃
TDP device : ionRocket (BioChromato)
Temperature program : RT → 600℃ (100℃/min)



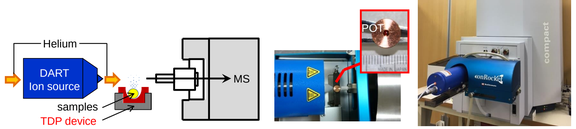


Fig.1 Thermal desorption/pyrolysis DART-MS system

Results and discussions

Standard samples

It was confirmed that a plurality of peaks having an interval (254.09 Da) corresponding to bisphenol A were detected in the 400-500 ℃. These peaks were considered to be oligomers of PC, because they were plotted on the horizontal lines in their KMD plot. From the EIC of several ions, the detection starting temperature was able to be divided at a boundary of 500 ℃. In detail, the compounds detected before 500 ℃ were considered to be “thermal desorption compounds”, and the compounds detected after 500 ℃ are “pyrolysis compounds”, respectively. The “thermal desorption compounds” are considered to retain the intact terminal structure. Moreover, these MS/MS spectra were presumed to be having the terminal structure specific to each synthesis method.

Industrial samples

It was confirmed that their terminal structure were identified by using the results of standard samples. And, these results were supported from the results by Py-GC/ MS and MALDI-MS.

A,B : p-t-butylphenoxy terminal and C,D : p-t-cumylphenoxy terminal

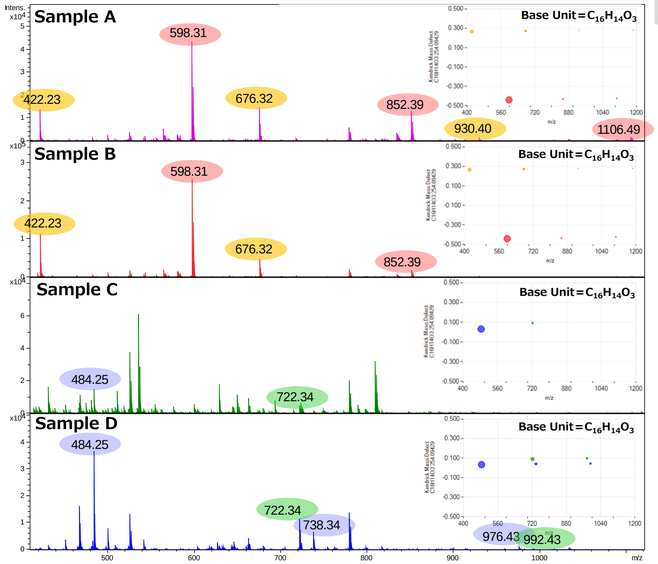


Fig.4 Results of four industrial samples (MS spectra of 400-500℃, KMD plots)

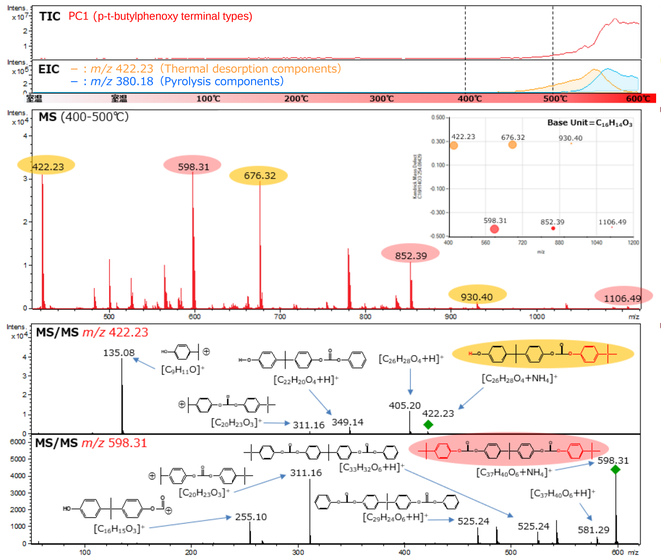


Fig.2 Results of PC1 (TIC, EIC, MS spectrum, MS/MS spectra)

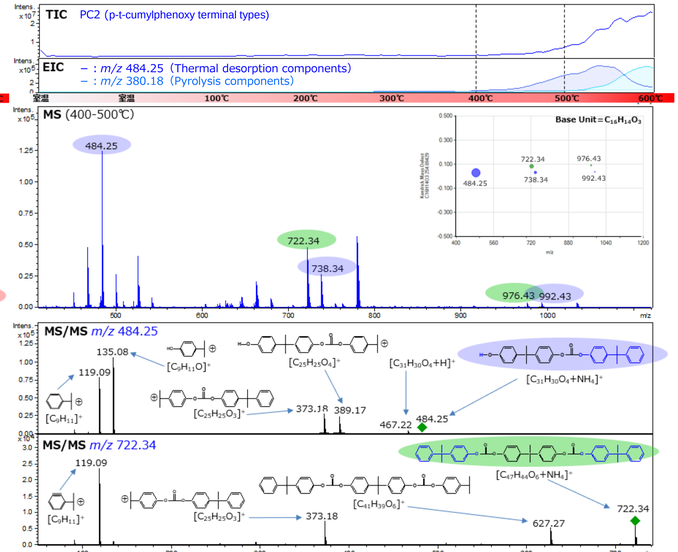


Fig.3 Results of PC2 (TIC, EIC, MS spectrum, MS/MS spectra)

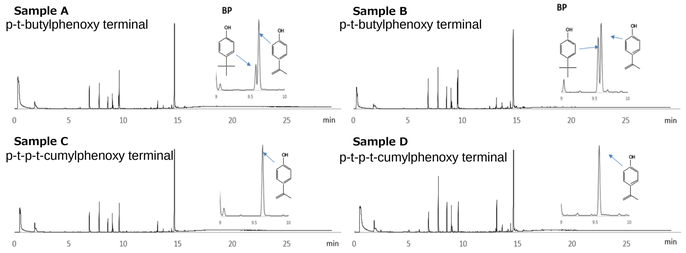


Fig.5 Pyrograms of four industrial samples*)

Pyrolyzer : 600℃, Column : UA-5 (30 m×0.25 mm id, 0.25 μm), Ionization : EI

* : S.Tsuge, H.Ohtani, and C.Watanabe; Pyrolysis-GC/MS Data Book of Synthetic Polymers, Elsevier (2011)

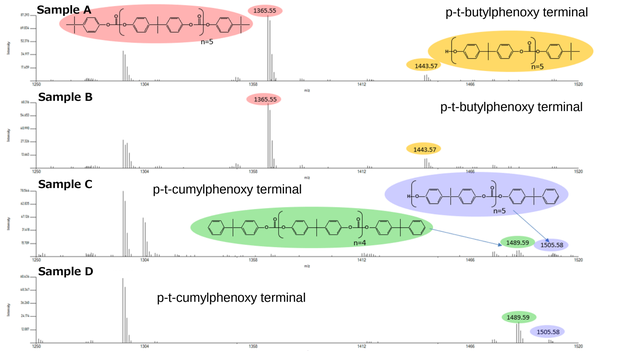


Fig.6 MALDI-MS spectra of four industrial samples

Solvent : THF, Matrix : DCTB, Cationization reagents : NaTFA

Conclusion

TDP/DART-MS utilize a combination of “vaporization of oligomer component” by heating at a temperature, “detection of molecular weight related ion” by soft ionization, and “structural analysis” by MS/MS spectra.
By using TDP/DART-MS, it is possible to simply analyze terminal structural and utilize identification of PC products without any pretreatment.
And it is expected to be useful for R&D and quality control.