Application of molecular characterization for fluorine polymers using thermal desorption/pyrolysis DART-MS

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Introduction

Fluorine polymers are utilized in the field of semiconductor technologies and automotive products due to their excellent chemical durability and mechanical properties. Molecular characterization of fluorine polymers is important because they are often copolymerized or modified to achieve higher performance, but it has been quite cumbersome. Even by pyrolysis (Py)-GC/MS, only monomer type can be barely determined. MALDI-MS is almost impossible to observe the mass spectra of fluorine polymers due to their nonpolarity.

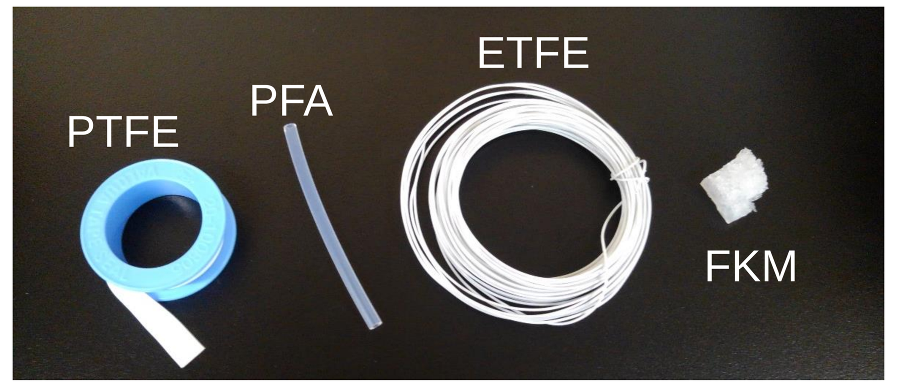
This presentation demonstrates the molecular characterization of fluorine polymers using a thermal desorption and pyrolysis (TDP)/DART-MS, which can rapidly detect both thermally desorbed intact oligomers and oligomeric pyrolysis products of polymers. By introducing Kendrick mass defect (KMD) analysis[1)] ,sequence analysis of fluorine copolymers can also be performed.

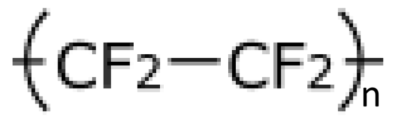
1) H.Sato, S.Nakamura, K.Teramoto, T.Sato; JASMS, 2014, 25(8), 1346-1355

Experimental

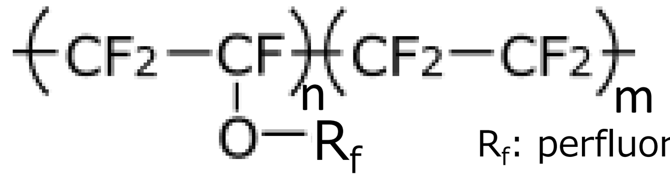
Samples

4 kinds of fluorine polymer products(commercial products)



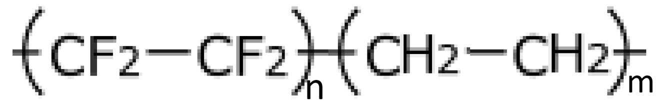


PTFE; Polytetrafluoroethylene

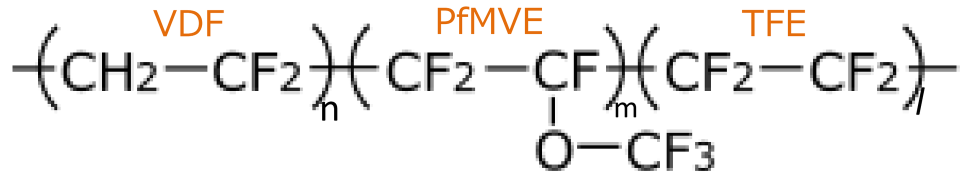


R_f: perfluoro alkane

PFA; Perfluoro alkoxyl alkane



ETFE; Ethylene-tetrafluoroethylene copolymer



FKM; (Vinylidenefluoride-perfluoromethylvinylether-tetrafluoroethylene) terpolymer

Analytical methods: TDP/DART-MS (Fig. 1)

Sample (ca. 0.2 mg) were used for measurement.

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

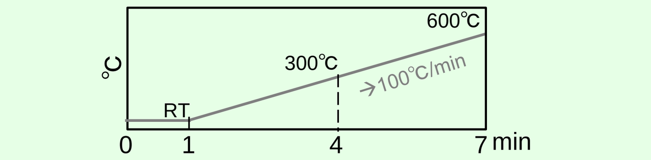


Fig. 2 Temperature program of TDP device

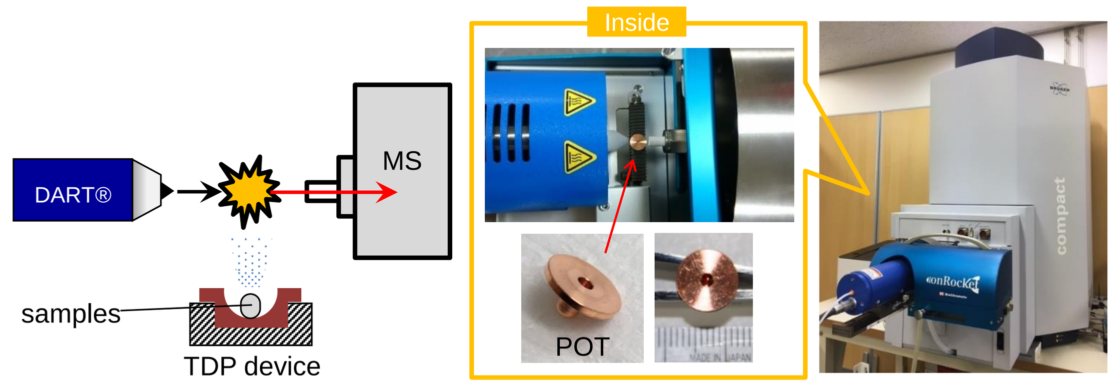


Fig.1 TDP/DART-MS system

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

Results and Discussions

For every fluorine polymer samples, oligomeric pyrolysis products could be successfully observed by TDP/DART-MS in negative ion mode. The KMD plot converted from each mass spectra showed that the oligomeric products contain CF_2 units as a base unit.

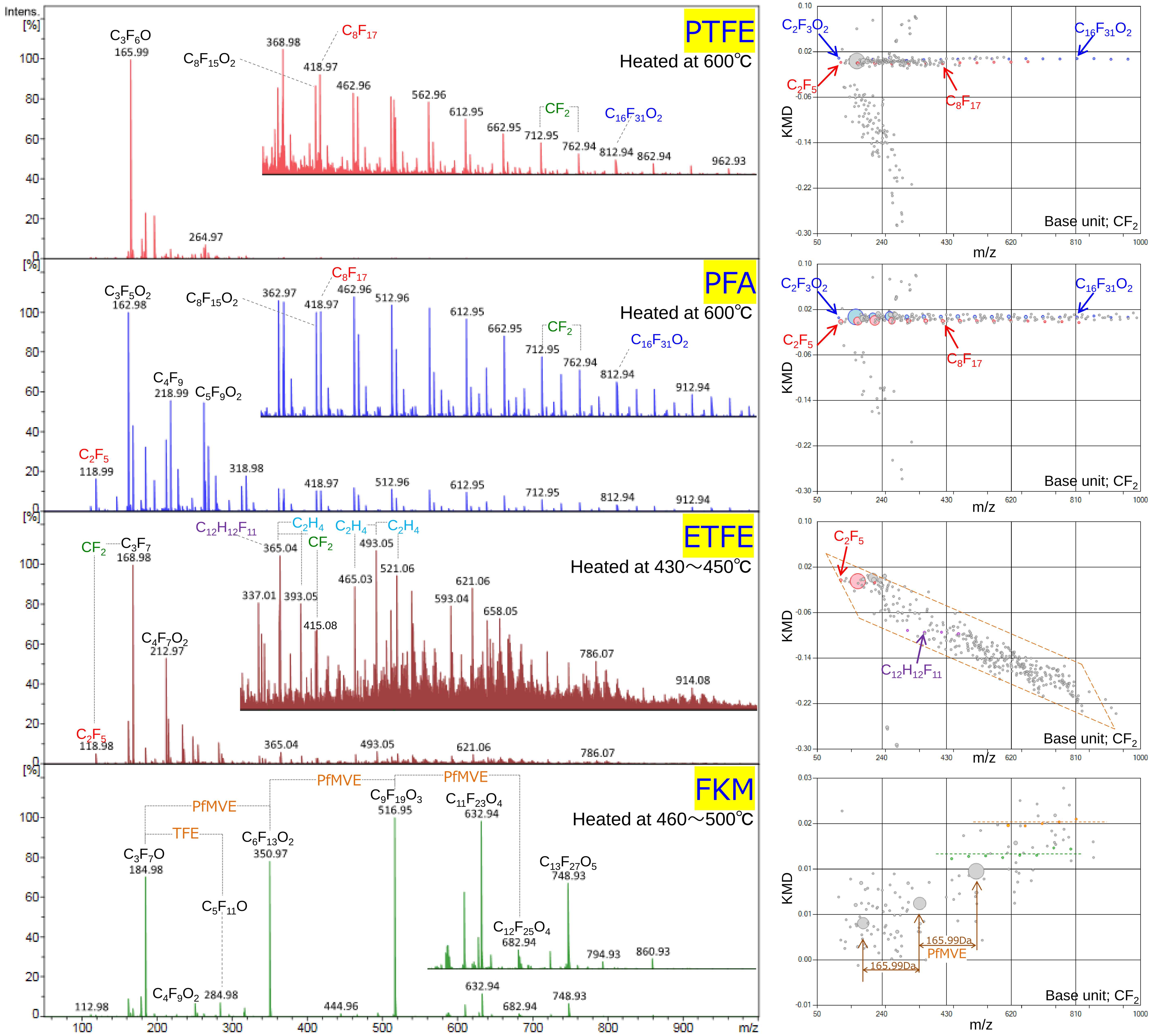


Fig. 3 TDP/DART(-)-MS spectra of at each sample's pyrolysis temperature and their KMD plots (Base unit; CF_2)

~ PTFE ~

The KMD plot of the PTFE sample depicted mainly two horizontal lines reflecting a CF_2 repeating unit. Interestingly, the products lined in the lower mass region could be identified as oxygen containing products. Such oxygen-containing products would be attributed to the chain terminal containing polymerization initiators or chain transfer agents.

~ PFA ~

Although the KMD plot of the PFA sample was similar to that of PTFE, mass spectral pattern of low molecular weight products would be a clue to discriminate between PTFE and PFA. The KMD pattern with almost no oxygen distribution suggested low contents of the perfluoro ether unit.

~ ETFE ~

The KMD plot of ETFE showed a parallelogram-like pattern reflecting CF_2 and CH_2 comonomer distribution. Short sequence of CF_2 indicated the ETFE sample would have high randomness.

~ FKM ~

Higher molecular weight products such as PfMVE-TFE (*m/z* 284.99), dimer of PfMVE (*m/z* 350.99) and trimer of PfMVE (*m/z* 516.98) could be detected. These products could not observe in the mass spectra obtained by Py-GC/MS. By using KMD analysis, the sequence distribution of comonomers and terminal structures were also characterized.

Conclusion

TDP/DART-MS enables measurement of not only low molecular weight but also oligomeric pyrolysis products of fluorine polymers. Therefore, it give us valuable clue to elucidate chemical structure of fluorine polymers (ex. chemical structural analysis of perfluoro alkane (R_f) of PFA, estimation of polymerization method by polymerization initiator and chain transfer agent and so on). Thus, it can contribute to further development of fluorine polymer analysis technology.