

The first Observation of high mass distribution of Polyrotaxane using MALDI-TOFMS and a high mass detector.

Shuuichi Nakaya¹; Kazuaki Kato²; Yuzo Yamazaki¹; Kohzo Ito²

¹Shimadzu Corporation, Kyoto, Japan; ²Department of Advanced Material Science, Graduate School of Frontier Science, The University of Tokyo, Japan.

Overview

- > Distribution of more than 100,000 MW of polyrotaxane is reported using MALDI-TOFMS equipped with a high mass detector.
- > It is shown that γ -PR forms a single-stranded structure predominantly, whereas an oligomer of other γ -PR was reported as a double-stranded.
- > In conjunction with NMR, the high mass detector in MALDI-TOFMS is a powerful tool to characterize the PR.

1: Introduction

Polyrotaxane (PR) is consisted with a linear polymer and slidable cyclic molecules, which are threaded on the polymer. Polyrotaxane gel is interlocked at ring components so that the polymer has a relative motion between the sliding rings along the main chain. Unique physical properties attributable to the relative motion of PR are greatly expected as a new industrial material. Whereas some successful studies of PR at low mass region have been reported with high resolving power of MS, an analysis of PR at high mass region is still difficult. We will report the first observation of PR at more than m/z 100,000 using MALDI-TOFMS equipped with a high mass detector, and discuss a structure of γ -CD-PR, which can form three possible structures due to a large cavity of γ -CD.

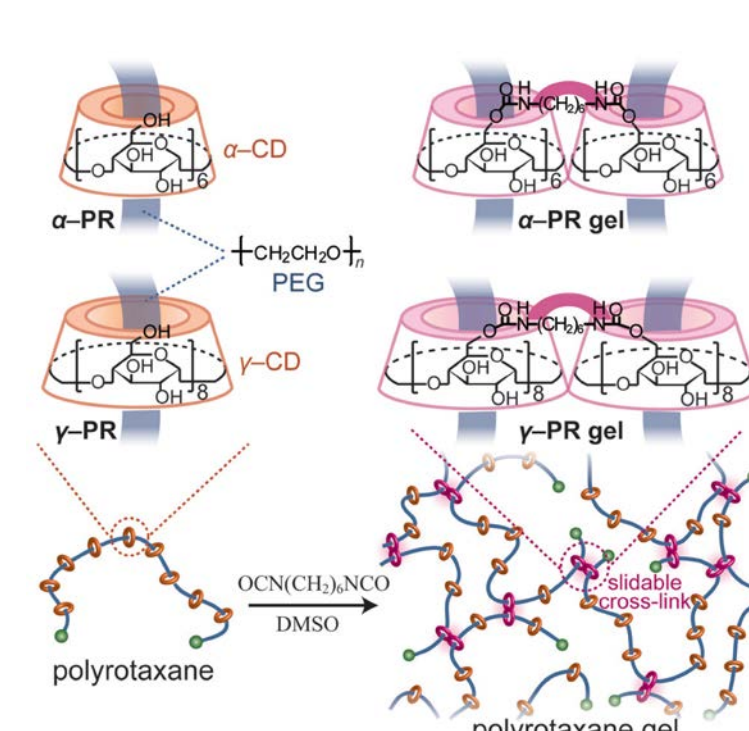


Fig.1 Polyrotaxanes and their cross-linked gels with differently sized cyclodextrins (CDs) ¹⁾

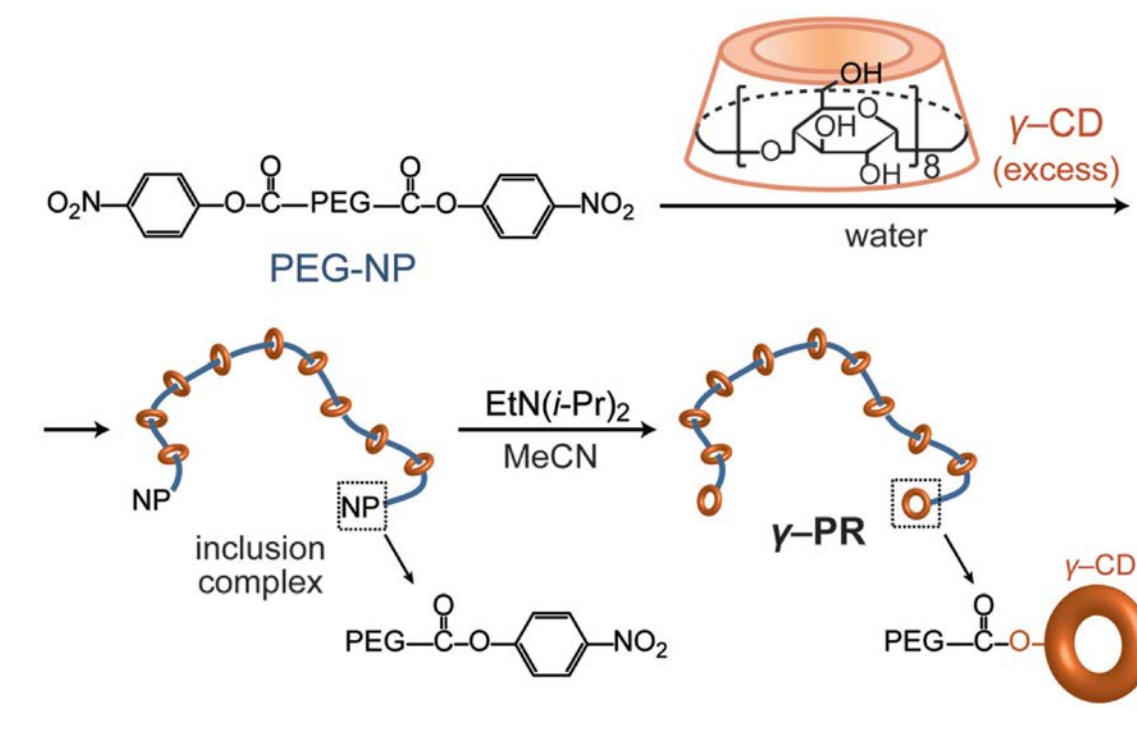


Fig.2 Synthetic scheme of γ -PR by end-capping via transesterification with untreated excess γ -CD ¹⁾

2: Methods

• Polyrotaxane

A PR composed of γ -cyclodextrin and polyethylene glycol ($M_n = 20k$) was synthesized according to a literature¹⁾, and other PRs composed of α -cyclodextrin and various M_n PEGs were obtained from Advanced Softmaterials Inc., Japan. The samples were dissolved in distilled water or chloroform/methanol=1/1, THF.

Polyrotaxane	M_n by SEC	M_n of PEG chain
APR35	100k	35k
SH1310P	180k	11k
SH2400P	400k	20k
SH3400P	700k	35k
γ -PR	87k	20k

Table. 1 M_n of polyrotaxanes estimated with SEC

3: Results

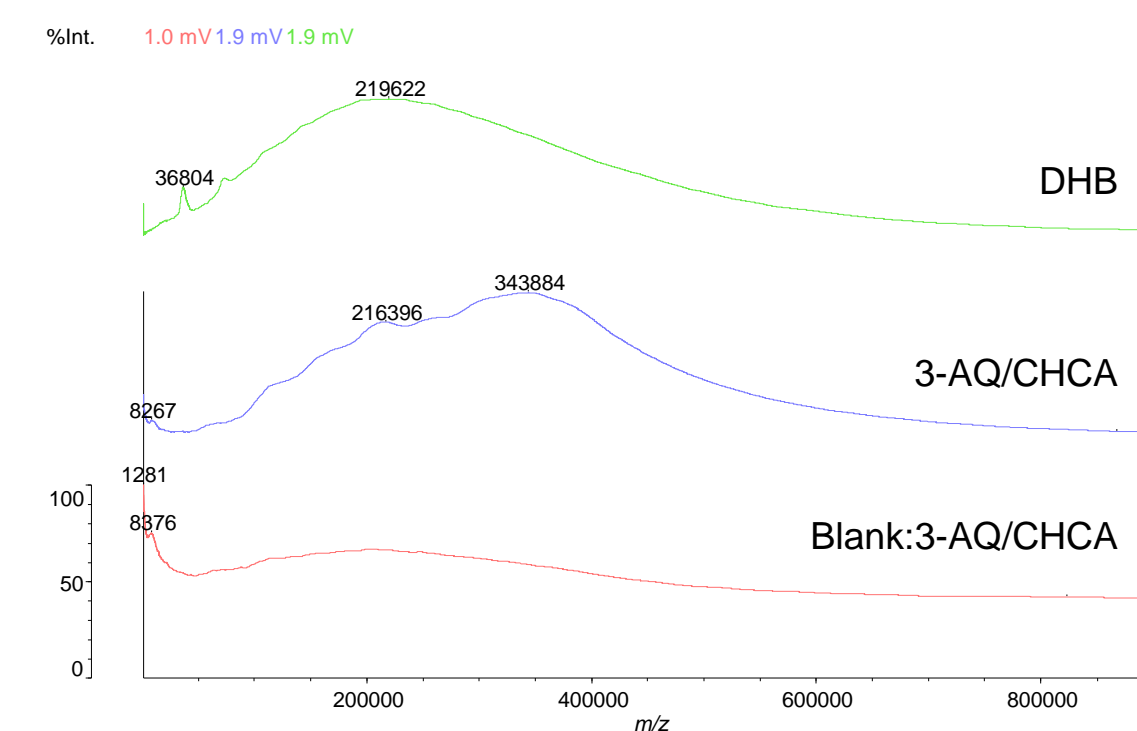


Fig.4 mass spectrum of SH1310P.

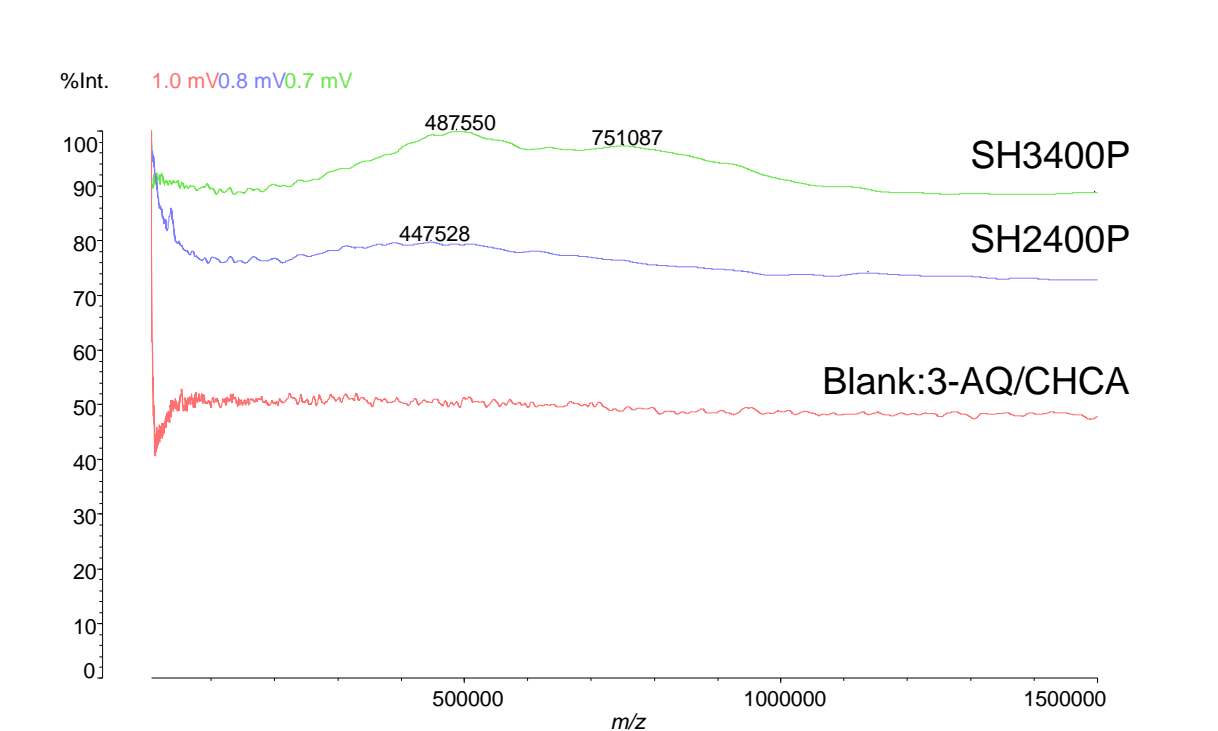


Fig.5 mass spectrum of SH2400P and SH3400P.

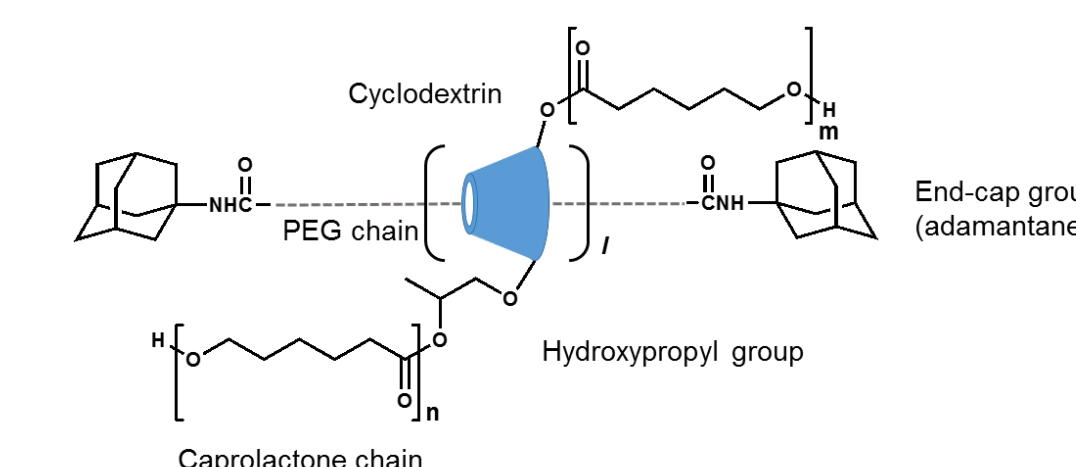


Fig.6 Structure of SH series.

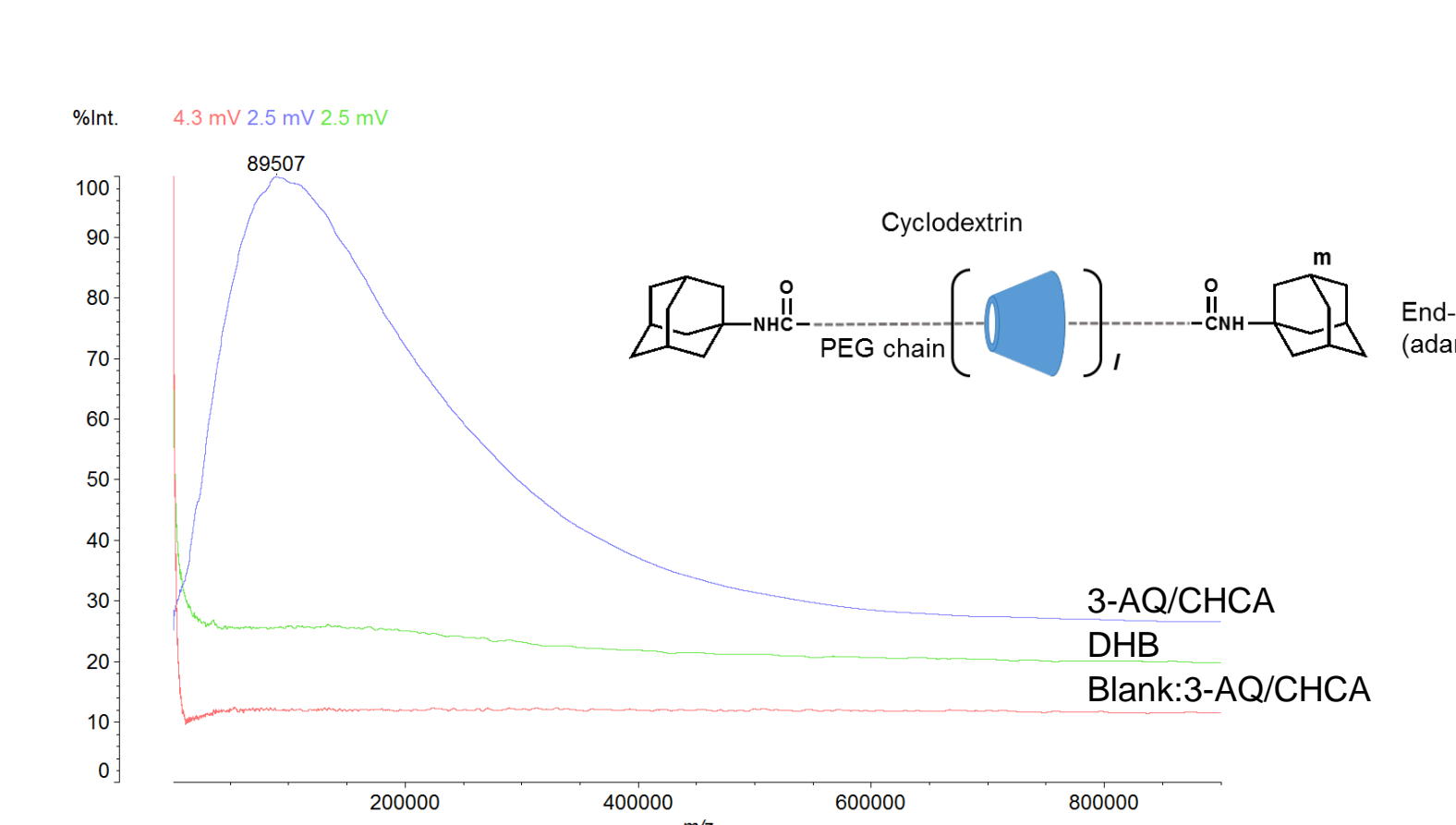


Fig.7 mass spectrum of APR35 and its structure.

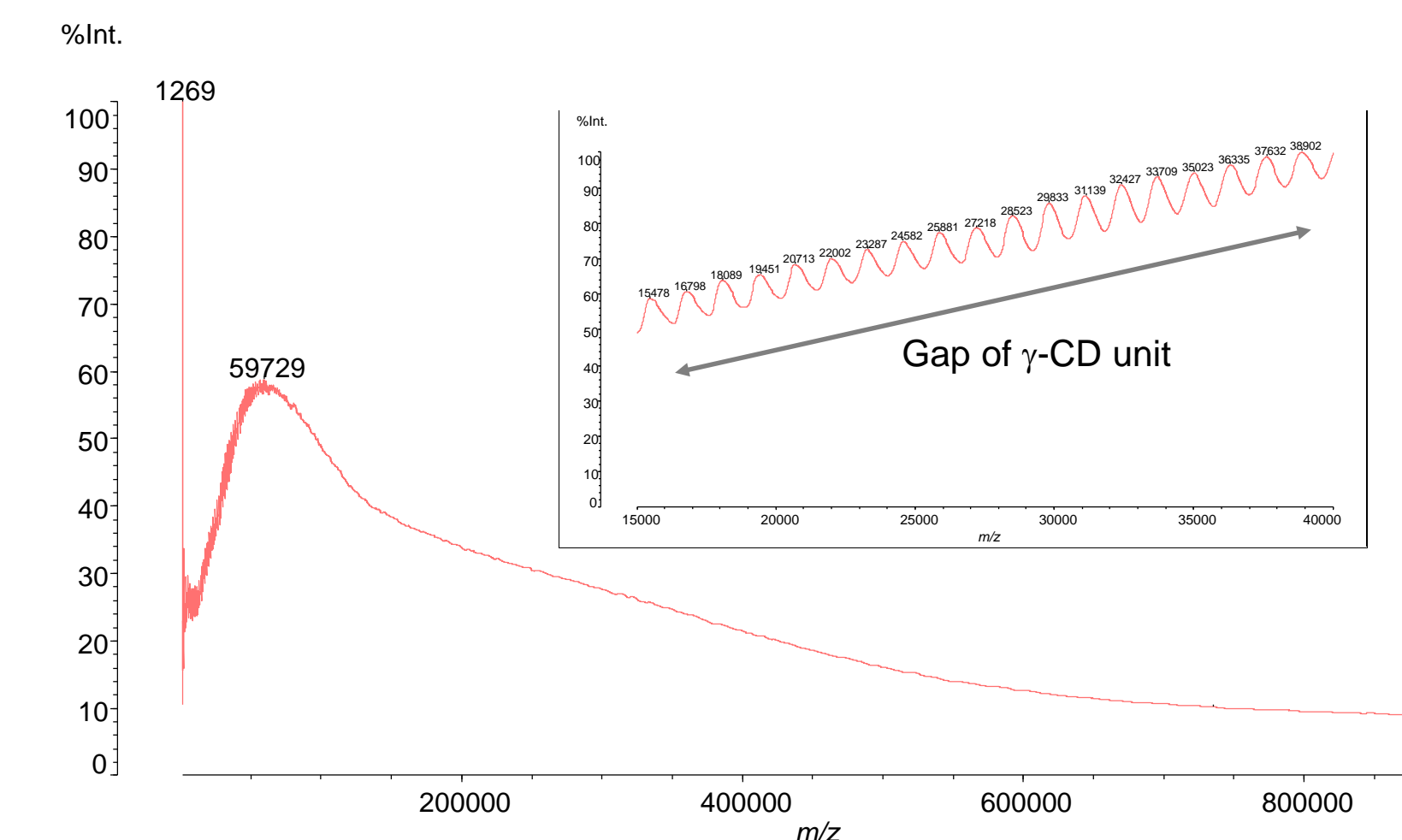


Fig.8 mass spectrum of γ -PR.

- MALDI-TOFMS and High Mass Detector
- MALDI-TOFMS: AXIMA-Performance (Shimadzu/Kratos)
- Measurement: Linear, positive mode
- Matrix: DHB and 3-aminoquinoline (3-AQ)/CHCA²⁾
- The dissolved samples were mixed with the matrix solution on a stainless MALDI plate
- Detector: HM3 high mass detection system (Covalex, Switzerland).

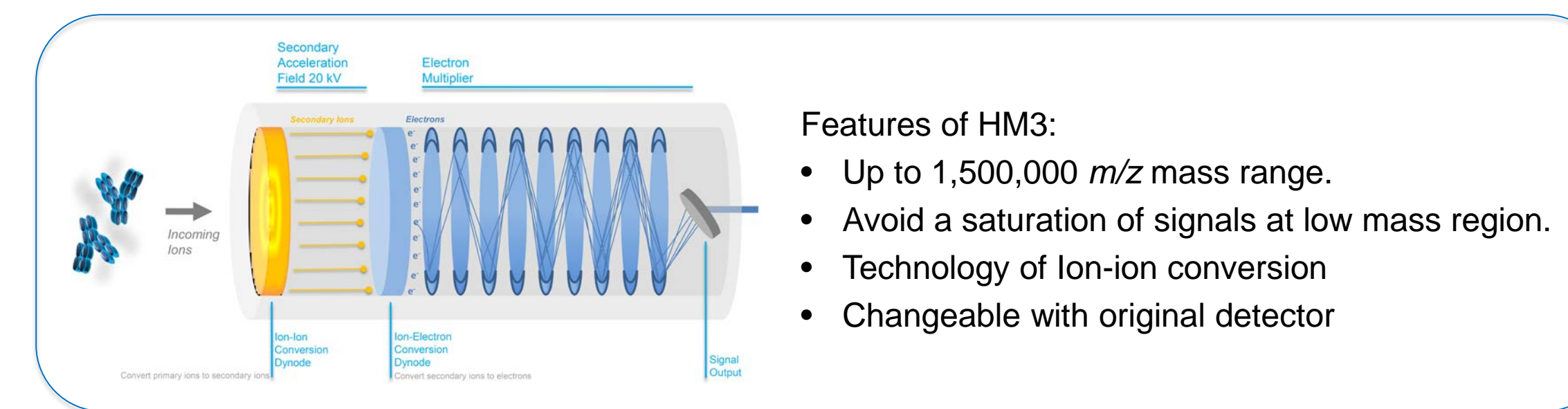


Fig.3 Principle of high mass detector.

Features of HM3:

- Up to 1,500,000 m/z mass range.
- Avoid a saturation of signals at low mass region.
- Technology of Ion-ion conversion
- Changeable with original detector

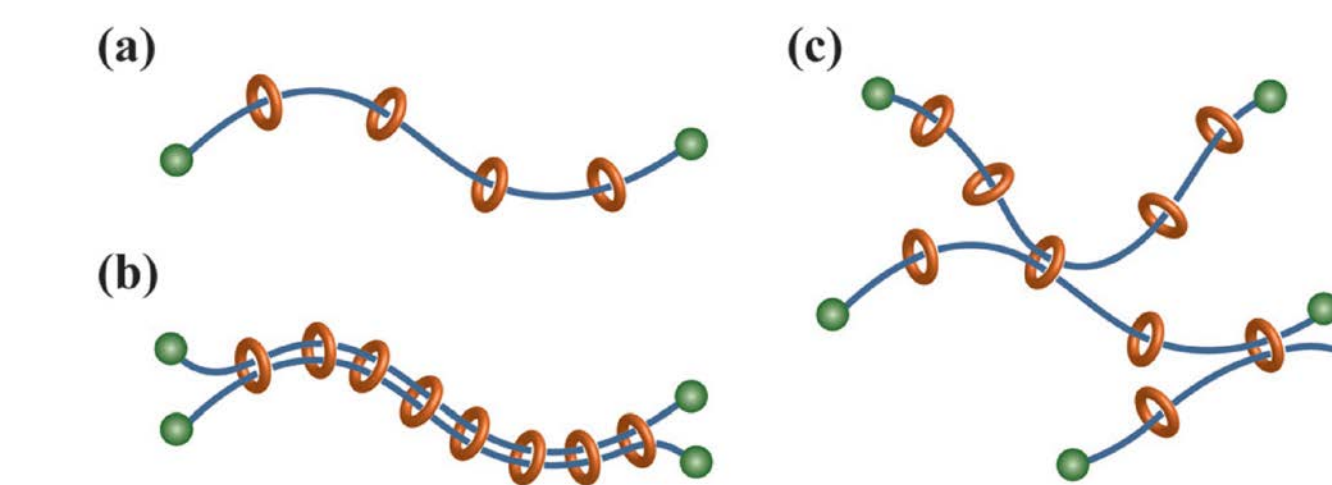
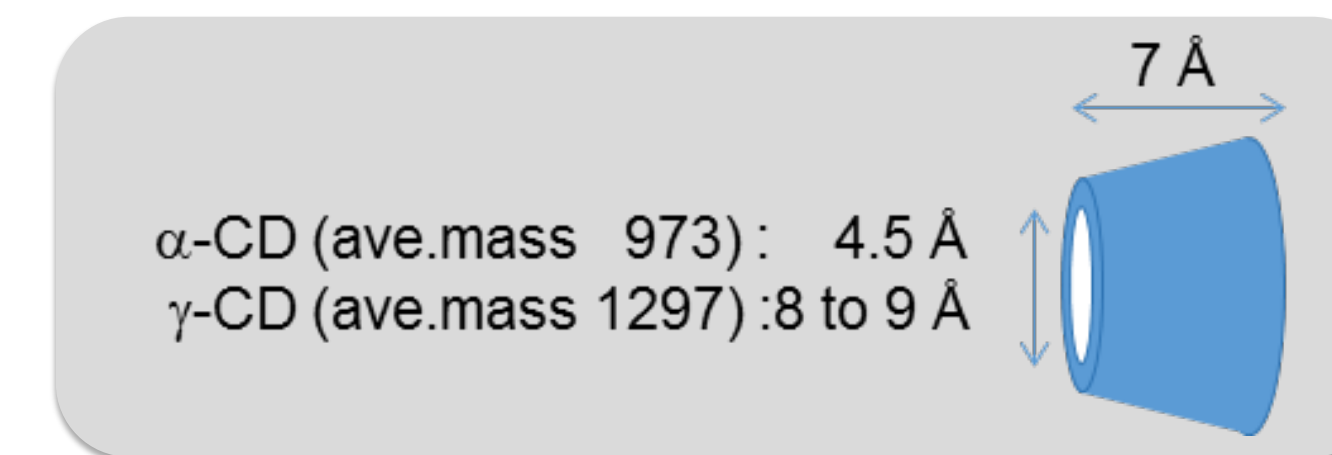


Fig.9 Dimension of α - and γ -CD³⁾, and three possible structures of γ -PR. Note that the molar ratio between PEG and γ -CD is the same for a),b),c).¹⁾

4: Conclusions

- ✓ Distribution of more than 100,000MW of polyrotaxane was shown using MALDI-TOFMS and high MS detector.
- ✓ A majority of γ -PR structure was thought to be a single strand formation, because an apex of the broaden signal and a predicted mass by using H¹- NMR are consisted with each other.
- ✓ An ionic liquid matrix was believed provisionally to be effective to ionize polyrotaxanes, but further investigation could be necessary to find more suitable matrices/conditions in relevance with various chemical structures of the polymer.

References;

- (1) Kato, K., et al., Polymer Chem., 2015, 6 :2241-2248.
- (2) Fukuyama, Y, et al., Rapid Commun. Mass Spectrom., 2012, 26: 2454-2460.
- (3) Harada, A., et al., Nature, 1994, 370:126-128.

Disclaimer: AXIMA-Performance and HM3 detector are intended for Research Use Only (RUO). Not for use in diagnostic procedures.