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Analysis of Recycled Polyesters using SEC-MALDI and Precipitation Method

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Overview

- Analysis of recycled polyester oligomers using SEC off-line MALDI system is demonstrated.
- The system combined with a precipitation technique is shown to be applicable to analysis of complicated mixtures of oligomers.
- Oligomers extracted from recycled PBT, PC, and PET are compared with high-grade counterparts.
- Two preparative methods, SEC-MALDI and precipitation method, are compared with each other, and "Pros and Cons" of the two method is discussed.

Methods

- SEC-off-line MALDI
  LC system; Prominence (Shimadzu Corp.)
  Fractionation; Accuspot (Shimadzu Corp.)
  Column; Showdex 1.0 mm x 250 mm x 2
  Flow rate of THF; 10 mL/min
  Matrix; Dithranol (20 mg/mL in $CHCl_3$)
  Cation; NaTFA (10 mg/mL in THF)
- MALDI-TOFMS
  AXIMA-Performance (Shimadzu Biotech / Kratos)
  Matrix; Dithranol (20 mg/mL in $CHCl_3$)
  Cation; NaTFA (10 mg/mL in THF)
- Data analysis
  "Polymers" (Shimadzu Biotech / Kratos)

Introduction

- Industrial demands for analysis of recycled polyesters are expected to increase.
- Oligomer analysis by MALDI-TOFMS is one of the powerful technique to evaluate the recycled polyesters.
- There are still some problematic issues of MALDI-TOFM in analysis of a broad polydispersity sample or in analysis of a complicated mixture due to mass discrimination observed in mass spectrum.
- While SEC-MALDI is one of the essential technique to solve the issues, precipitation method is thought to be more suitable for multi-sample analysis because of shorter required time than SEC-MALDI.
- The two preparative methods were applied to analysis of oligomers extracted from recycled PBT, PC, and PET, and examined their usability.

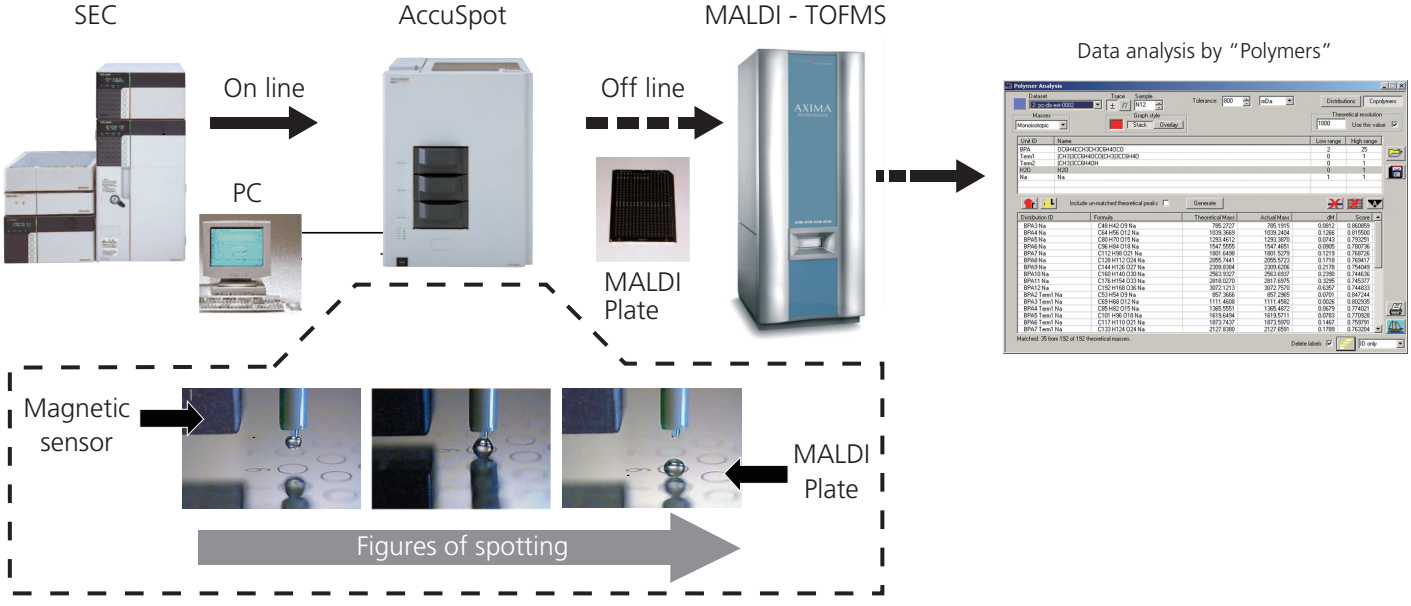


Fig. 1 Work-flow of SEC-MALDI

Analysis of Recycled Polyesters using SEC-MALDI and Precipitation Method

Results

Analysis of PBT (polybutylene terephthalate) by precipitation and MS

250mg in 2.5mL HFIP/$CHCl_3$

↓

Precipitation of H.W. polymer
10-fold volume of acetonitrile

↓

Filter

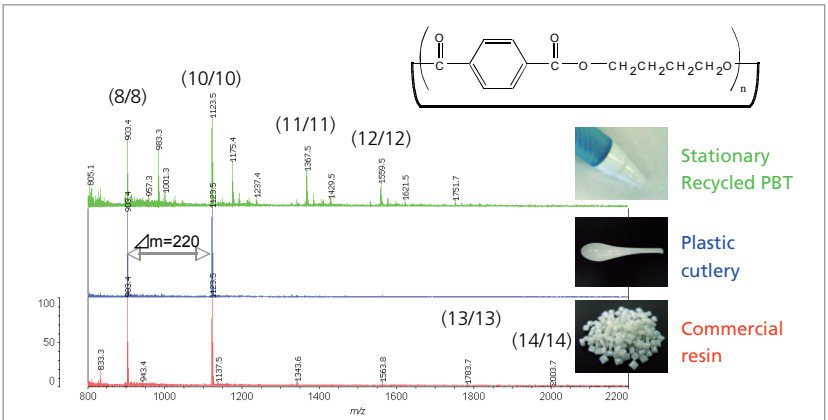
↓

Soluble compounds in acetonitrile

↓

MALDI-TOFMS

Fig. 2 Extraction of PBT oligomer



legend：(m/n);Cyclic Oligomers m; number of terephtalate n;number of butylene glycol

Fig. 3 Mass spectra of PBT oligomers

Analysis of PC (polycarbonate) by precipitation and MS

1000mg in 1.0mL $CHCl_3$

↓

Precipitation of H.W. polymer
10-fold volume of acetonitrile

↓

Filter

↓

Soluble compounds in acetonitrile

↓

MALDI-TOFMS & MS/MS

Fig. 4 Extraction of PC oligomer

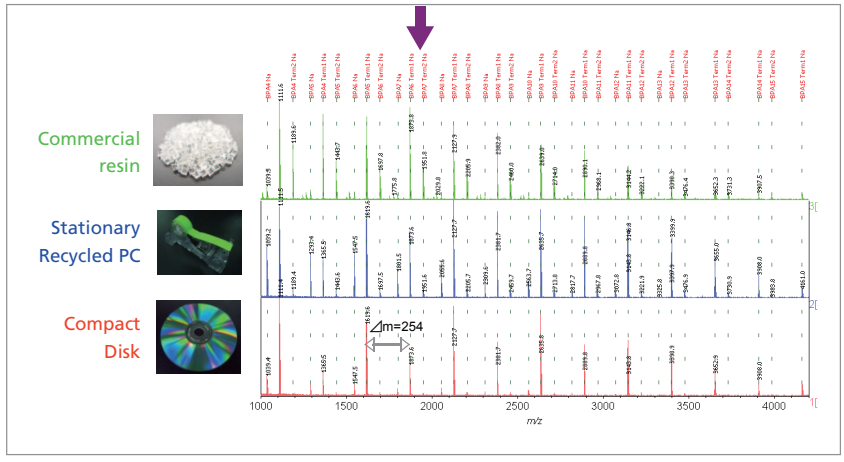


Fig. 5 Mass spectra of PC oligomers

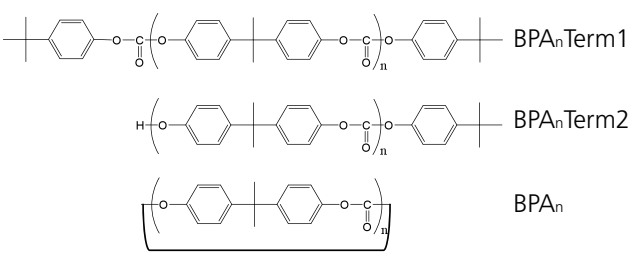


Fig. 6 Various end-terminal groupsof PC oligomer

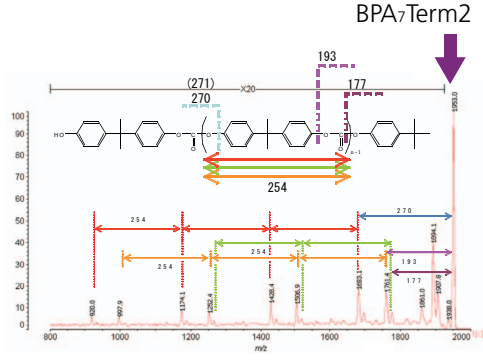


Fig. 7 CID-MS/MS of a PC oligomer

Analysis of Recycled Polyesters using SEC-MALDI and Precipitation Method

Analysis of PET (polyethylene terephthalate) by precipitation and SEC-MALDI

200mg in 2.0mL + 8mL $CHCl_3$

↓

Precipitation of H.W. polymer
10-fold volume of THF

↓

Filter

↓

Soluble compounds in THF

↓

MALDI-TOFMS　　SEC-MALDI

Fig. 8 Extraction of PET oligomer

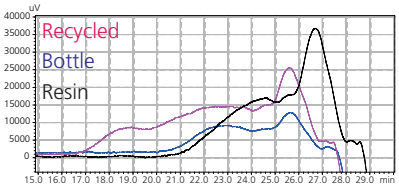


Fig. 9 SEC chromatograph of PET oligomers

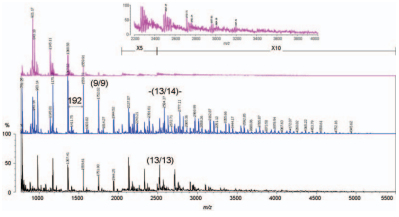


Fig. 10 Mass spectra of PET oligomers, after the extraction.

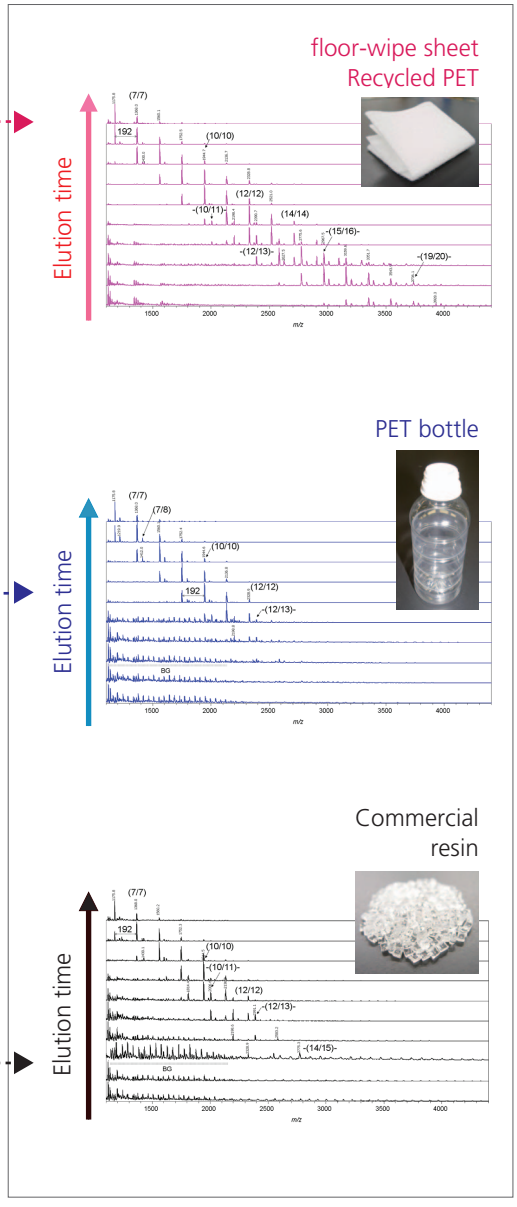


Fig. 11 SEC-MALDI of PET oligomers

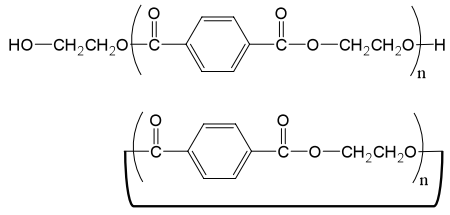


Fig.12 Oligomers observed dominantly

ID Formula	Chemical Formula	Theoretical Mass (ma)	Origomer PET	Origomer Bottle	Origomer regenerated
C60 H48 O24 Na	TA6 EG6 Na	1175.24	●	●	●
C60 H50 O25 Na	TA6 EG6 Na H2O	1193.25			
C62 H52 O25 Na	TA6 EG7 Na	1219.27		●	
C62 H54 O26 Na	TA6 EG7 Na H2O	1237.28			
C70 H56 O28 Na	TA7 EG7 Na	1367.28	●	●	●
C70 H58 O29 Na	TA7 EG7 Na H2O	1385.30			
C72 H60 O29 Na	TA7 EG8 Na	1411.31		●	
C72 H62 O30 Na	TA7 EG8 Na H2O	1429.32	●		
C80 H64 O32 Na	TA8 EG8 Na	1559.33	●	●	●
C80 H66 O33 Na	TA8 EG8 Na H2O	1577.34			
C82 H68 O33 Na	TA8 EG9 Na	1603.35		●	
C82 H70 O34 Na	TA8 EG9 Na H2O	1621.36	●		
C90 H72 O36 Na	TA9 EG9 Na	1752.38	●	●	●
C90 H74 O37 Na	TA9 EG9 Na H2O	1770.38			
C92 H76 O37 Na	TA9 EG10 Na	1796.40		●	
C92 H78 O38 Na	TA9 EG10 Na H2O	1814.41	●		
C100 H80 O40 Na	TA10 EG10 Na	1944.42	●	●	●
C100 H82 O41 Na	TA10 EG10 Na H2O	1962.43			
C102 H84 O41 Na	TA10 EG11 Na	1988.44			
C102 H86 O42 Na	TA10 EG11 Na H2O	2006.45	●		●
C110 H88 O44 Na	TA11 EG11 Na	2136.46	●	●	●
C110 H90 O45 Na	TA11 EG11 Na H2O	2154.47			
C112 H92 O45 Na	TA11 EG12 Na	2180.48			
C112 H94 O46 Na	TA11 EG12 Na H2O	2198.50	●		
C120 H96 O48 Na	TA12 EG12 Na	2328.50	●	●	●
C120 H98 O49 Na	TA12 EG12 Na H2O	2346.51			
C122 H100 O49 Na	TA12 EG13 Na	2372.53			
C122 H102 O50 Na	TA12 EG13 Na H2O	2390.54	●		●
C130 H104 O52 Na	TA13 EG13 Na	2520.54			●
C130 H106 O53 Na	TA13 EG13 Na H2O	2538.55			
C132 H108 O53 Na	TA13 EG14 Na	2564.57			
C132 H110 O54 Na	TA13 EG14 Na H2O	2582.58	●		●
C140 H112 O56 Na	TA14 EG14 Na	2712.58			●
C140 H114 O57 Na	TA14 EG14 Na H2O	2730.59			
C142 H116 O57 Na	TA14 EG15 Na	2756.61			
C142 H118 O58 Na	TA14 EG15 Na H2O	2774.62	●		●
C150 H120 O60 Na	TA15 EG15 Na	2904.62			●
C150 H122 O61 Na	TA15 EG15 Na H2O	2922.64			
C152 H124 O61 Na	TA15 EG16 Na	2948.65			
C152 H126 O62 Na	TA15 EG16 Na H2O	2966.67			●
C160 H128 O64 Na	TA16 EG16 Na	3096.67			
C160 H130 O65 Na	TA16 EG16 Na H2O	3114.68			
C162 H132 O65 Na	TA16 EG17 Na	3140.69			
C162 H134 O66 Na	TA16 EG17 Na H2O	3158.70			●
C170 H136 O68 Na	TA17 EG17 Na	3289.71			
C170 H138 O69 Na	TA17 EG17 Na H2O	3307.73			
C172 H140 O69 Na	TA17 EG18 Na	3333.74			
C172 H142 O70 Na	TA17 EG18 Na H2O	3351.75			●
C180 H144 O72 Na	TA18 EG18 Na	3481.76			
C180 H146 O73 Na	TA18 EG18 Na H2O	3499.77			
C182 H148 O73 Na	TA18 EG19 Na	3525.78			
C182 H150 O74 Na	TA18 EG19 Na H2O	3543.79			●
C190 H152 O76 Na	TA19 EG19 Na	3673.80			
C190 H154 O77 Na	TA19 EG19 Na H2O	3691.81			
C192 H156 O77 Na	TA19 EG20 Na	3717.82			
C192 H158 O78 Na	TA19 EG20 Na H2O	3735.83			●
C200 H160 O80 Na	TA20 EG20 Na	3865.84			
C200 H162 O81 Na	TA20 EG20 Na H2O	3883.85			
C202 H164 O81 Na	TA20 EG21 Na	3909.87			
C202 H166 O82 Na	TA20 EG21 Na H2O	3927.88			

□ White column ; cyclic oligomer
▨ Pale yellow ; linear oligomer

Table 1 Comparison of oligomers

◆Legend：-(m/n)-;Linear Oligomers (m/n);Cyclic Oligomers m; number of terephtalate n;number of ethylene glycol

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Conclusions

- Polyester oligomers extracted from recycled polymers were analyzed using MALDI-TOFMS and SEC-MALDI.
- The oligomer extracted from the recycled PET polymer was so complicated mixture that SEC-MALDI combined with the precipitation technique was necessary to analyze it. The recycled oligomer extracted in THF probably involves other constituents.
- In the case of analysis of PBT and PC, only the extraction using the participation technique is effective to eliminate mass discrimination partially. This extraction procedure could be suitable to perform a multi-sample analysis, because the procedure takes a shorter work-time than SEC-MALDI.
- CID-MS/MS could be applicable to confirm a chemical structure of end-terminal group in an oligomer.
- The software was very helpful to assign observed *m/z* to oligomers, which have various end-terminal groups.

Reference

1. "MALDI Mass Spectrometry for Synthetic Polymer Analysis" , edited by Liang Li, 2009.

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