



End-group Analysis of Optical Media Material Polycarbonate by MALDI-TOF MS

We performed end-group analysis of polycarbonate using the Bruker MALDI-TOF MS autoflex maX. Results indicated usefulness for composition confirmation, quality control, and identification of synthetic approach.

Summary

This application note will introduce an example of end-group analysis for polycarbonate, which is used as a material for commercial CD-Rs.

Keywords:
autoflex maX, polytools,
polymer, polycarbonate

Introduction

Polycarbonates are general-purpose engineering plastics with advanced physical characteristics in terms of transparency, impact resistance, and heat resistance which are used not only in personal items such as CDs, DVDs and sunglasses, but also for building materials and bulletproof glass. There are two main methods for synthesizing polycarbonate: the phosgene method and the transesterification method. Traditionally, most polycarbonates were synthesized by the phosgene method using phosgene (a hazardous substance) rather than the transesterification method, as the transesterification method was considered to produce inferior quality polycarbonate. However, in recent years, with the increased interest in green chemistry, the development of methods of synthesizing polycarbonates using the transesterification method has been vigorously pursued. In this application note, we describe a case study in which we used MALDI-TOF MS to analyze polycarbonate used as a material for CD-Rs currently available on the market and discuss the synthesis method with reference to the data on end-groups that was obtained. MALDI-TOF MS has conventionally been widely used for molecular weight determination and identification of proteins and peptides, mainly in the

field of proteomics. However, in recent years, its application in the material and chemical industry fields has dramatically increased, and it has come to be used in analyzing synthetic polymers and additives. Specifically, MALDI-TOF MS is considered very advantageous when analyzing synthetic polymers as it can cover a relatively wide molecular weight range and its spectra tend to be simple as it tends not to generate multiply charged ions. It even allows for the observation of mixtures with different end-groups as discontinuous peaks provided their masses (molecular weights) differ, meaning that mixtures can be clearly identified and it is relatively easy to obtain information that can be difficult to obtain using analytical methods other than mass spectrometry.

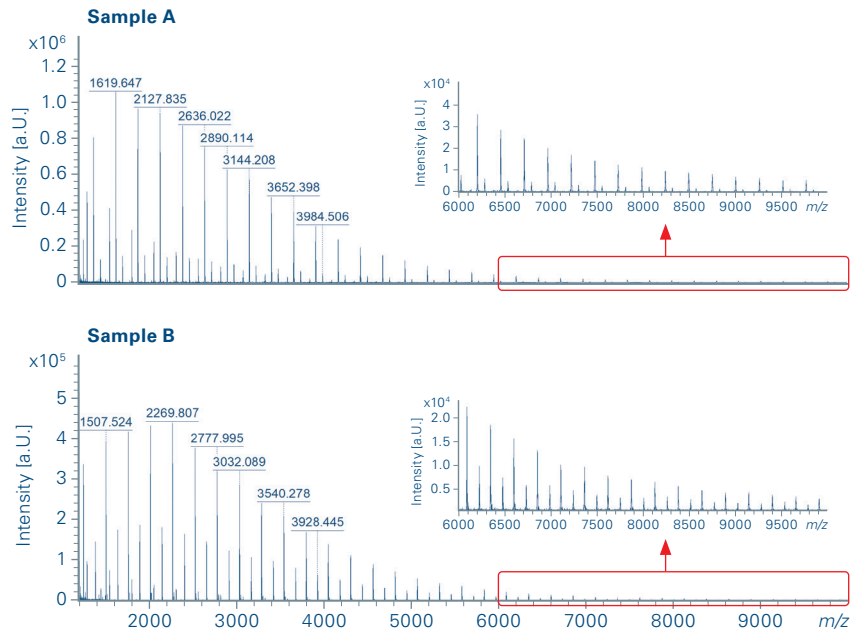


Figure 1
Mass spectra of polycarbonate (PC) used in two types of CD-R.
 In the mass range measured here, signals were detected up to the upper limit of m/z 10,000 for both samples, indicating that they have wide distribution.

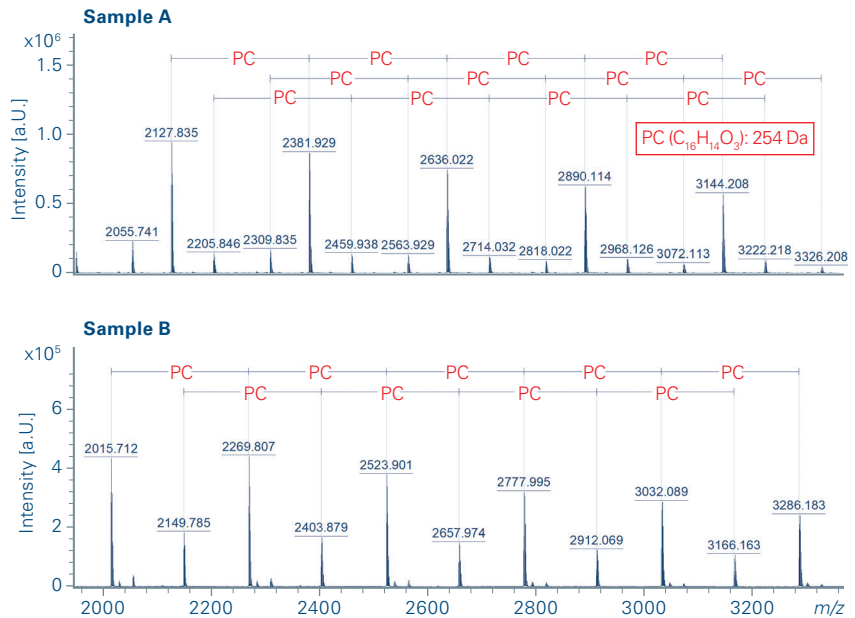


Figure 2
Mass spectra of polycarbonate (PC) used in two types of CD-R.
 Enlarged mass spectra of polycarbonate (PC) used in two types of CD-R. The signal spacing for both samples was 254 Da, which corresponds to polycarbonate (PC), but the values differ between the samples, suggesting different end-groups.

Sample Preparation

Small pieces were cut from two commercial CD-Rs (Samples A and B) and made into 20 mg/mL solutions in tetrahydrofuran, respectively. These solutions were mixed with matrix solution (DCTB 20 mg/mL in THF) and cationizing agent solution (sodium trifluoroacetate 2 mg/mL in THF), dropped onto a target plate (MTP 384 Ground Steel), and dried.

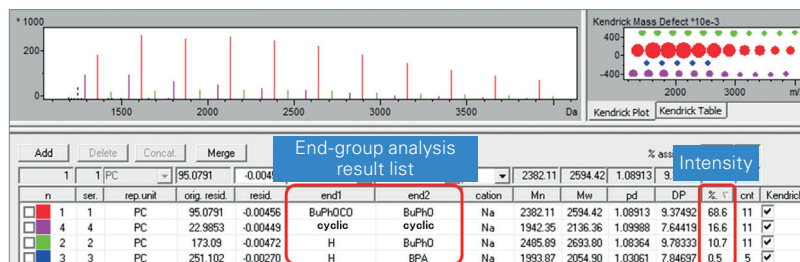
MALDI-TOF Measurement Conditions

An autoflex maX was used for the mass spectrometer. This model is capable of high-speed measurement with a 2000 Hz laser and has an improved dynamic range with a 10-bit digitizer. Measurements were taken in Positive Reflector mode. The measured data was analyzed using the polymer spectrum analysis software PolyTools 2.0 after peak picking using flexanalysis software.

Analysis Results

Figure 1 shows the measurement results of two samples, and Figure 2 is an enlarged image. Signals with different degrees of polymerization were detected at equal intervals in each case. The interval (254 Da) suggests that it is a polycarbonate with bisphenol A in the structure. However, the mass (m/z) of each signal differs in the two samples, suggesting different end-group structures. Figure 3 shows the results of end-group analysis obtained by loading the spectra into PolyTools 2.0. See Figure 4 for the end-group notation and structure

Sample A



Sample B

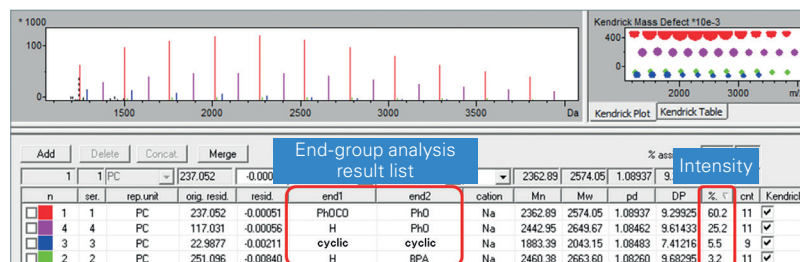


Figure 3

End-group analysis results from PolyTools 2.0. Sample A is characterized by butylphenol as an end-group and Sample B is characterized by being assigned phenol. Since only the low-molecular-weight regions were targeted for analysis in this application note, the figures shown for average molecular weights are thought to be lower than their true values.

	Notation in polytools (end1-end2)	Intensity (%)	Structure
Sample A	BuPhOCO - BuPhO	68.6	
	cyclic - cyclic	16.6	
	H - BuPhO	10.7	
	H - BPA	0.5	
Sample B	PhOCO - PhO	60.2	
	H - PhO	25.2	
	cyclic - cyclic	5.5	
	H - BPA	3.2	

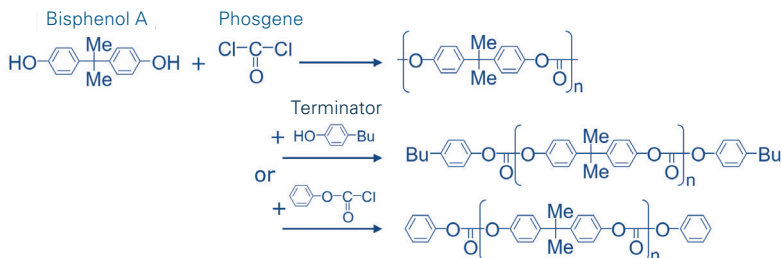
Figure 4

Notation in Polytools 2.0 and structures of end-groups

from PolyTools 2.0. The predominant end-group in Sample A is butylphenol and phenol in Sample B. From this, we can infer that Sample A was synthesized by the phosgene method using butylphenol as a terminator.

In addition, Sample B appears to have been synthesized either by the transesterification method using diphenyl carbonate, or by the phosgene method using phenyl chloroformate as a terminator or terminal modifier (Figure 5).

Phosgene method



Transesterification method

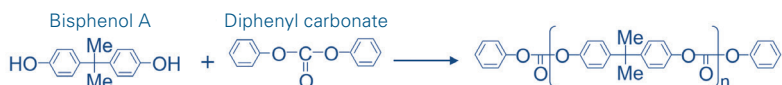


Figure 5:
Polycarbonate synthesis method.
Top: Phosgene method, Bottom: Transesterification method.

Conclusion

Using MALDI-MS allowed us to analyze the polycarbonate used in the CD-Rs and obtain information on the end-groups. This information is useful for determining the synthesis method and can be applied in composition confirmation, quality control, and analyzing other companies' products using the same method. We anticipate that it will be possible to make effective use of this method in various analysis applications for synthetic polymer samples.

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Bruker Switzerland AG

Fällanden · Switzerland
Phone +41 44 825 91 11

Bruker Scientific LLC

Billerica, MA · USA
Phone +1 (978) 663-3660

