

High throughput characterization of biopolyol using DART-MS with ultra-fast polarity switching

ASMS 2013 MP36-733

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1. Introduction

Many synthetic chemical products depend on petroleum for starting materials, but petroleum is a limited natural resource. Therefore, it is very important to develop chemical products from renewable sources such as biomass.

At Kyoto University, Shiraishi's group has been studying the conversion of biomass into liquid with high reactivity. The chemical and physical properties of liquefied biomass materials must be evaluated from various viewpoints.

DART (Direct Analysis in Real Time), a direct atmospheric pressure ionization source, is capable of analyzing chemical products with little or no sample preparation and is also useful for resin products' analysis because there is no need for dissolution. By combining the DART ion source with a quadrupole mass spectrometer, the characteristic chemical structures of propylene oxide (PO)-added liquefied starch (biopolyol) were successfully determined.

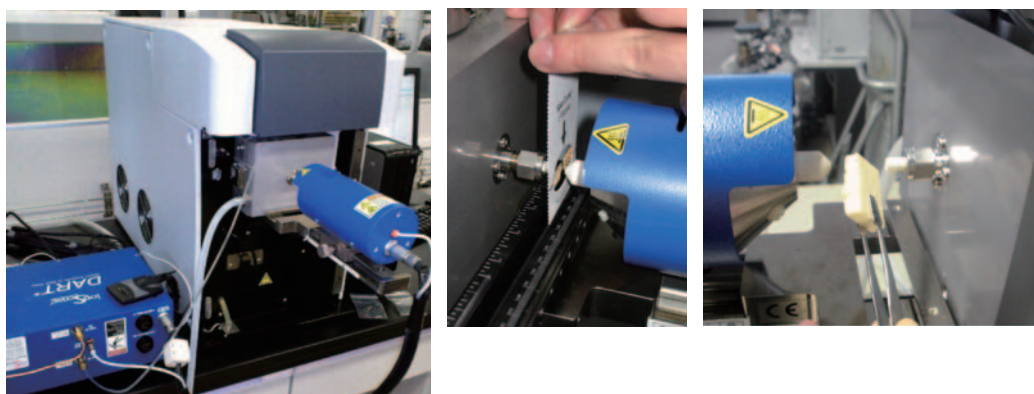


Fig. 1 DART-SVP ion source LCMS-2020

2. Methods and Materials

Corn starch, sucrose, liquefied corn starch, PO-added liquefied corn starch (biopolyol) and reagents were spotted on a metal mesh to scan with the DART beam. Foam made from PO-added liquefied starch, polyisocyanates and other samples were placed into the DART stream with forceps. The DART-SVP ion source (IonSense Inc., MA, USA) was mounted onto either a single quadrupole mass spectrometer LCMS-2020 or hybrid iontrap time-of-flight

mass spectrometer LCMS-IT-TOF MS (Shimadzu Corporation, Kyoto, Japan). Ultra-fast polarity switching was utilized on the mass spectrometer to collect full scan data. LCMS-2020 can achieve a polarity switching time of 15 msec and the scanning speed of up to 15000 u/sec, therefore the loop time can be set at less than 1 second despite the relatively large scanning range of 50-1500 u.

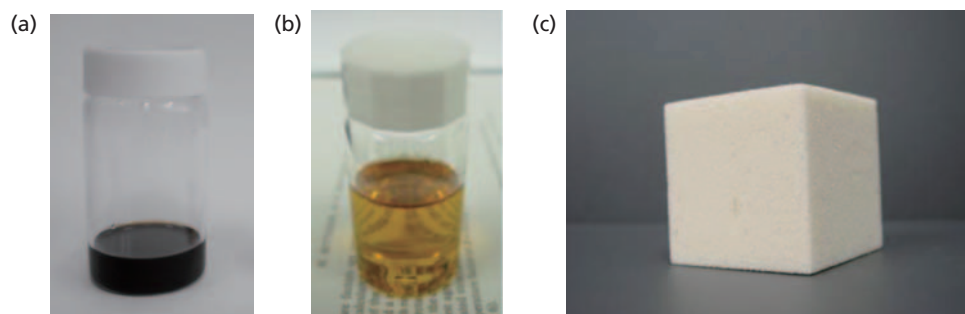


Fig. 2 Pictures of (a) liquefied corn starch, (b) PO-added liquefied corn starch (biopolyol) and (c) foam made from biopolyol

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3. Results

3-1. Starch

First, starch as the raw material biomass was analyzed by DART-LCMS-2020. Starch is a polymer consisting of alpha glucose (C₆H₁₂O₆, MW180). The abundant signal at *m/z* 342 in positive ion mode was observed. It was thought that the signal at *m/z* 342 could be assigned to [Disaccharide]⁺

or [Disaccharide +NH₄-H₂O]⁺. In order to confirm this, we analyzed sucrose by DART-LCMS-IT-TOF. The result shows that the signal at *m/z* 342 is [Disaccharide +NH₄-H₂O]⁺ (Table 1). It was found that sugar tended to be detected as [M +NH₄-H₂O]⁺.

Table1 Theoretical value and measured value of disaccharide

	Theoretical <i>m/z</i>	Measured <i>m/z</i>	Error (mDa)
M ⁺	342.1157	342.1393	23.6
[M+NH ₄ -H ₂ O] ⁺	342.1395	342.1393	0.2

Mass calibration was performed by internal standard

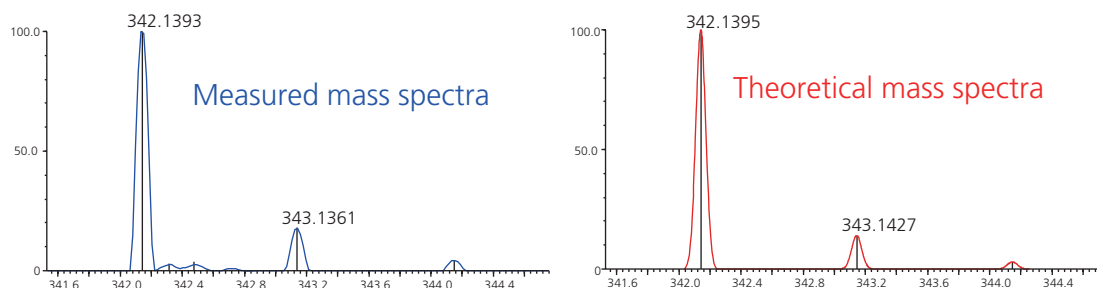


Fig. 3 Mass spectra in positive ion mode of Sucrose

Therefore, the signal at *m/z* 342 (Fig. 4) can be assigned to [Disaccharide+NH₄-H₂O]⁺. The signal at *m/z* 504 in positive ion mode also can be assigned to [Trisaccharide +NH₄-H₂O]⁺. The spectrum in negative mode shows

characteristic signal interval of 162 u. These spectra were more dominant in both polarities at temperature setting of 500°C than 350°C. It was therefore determined that 500°C was the suitable temperature for analysis of biopolyol.

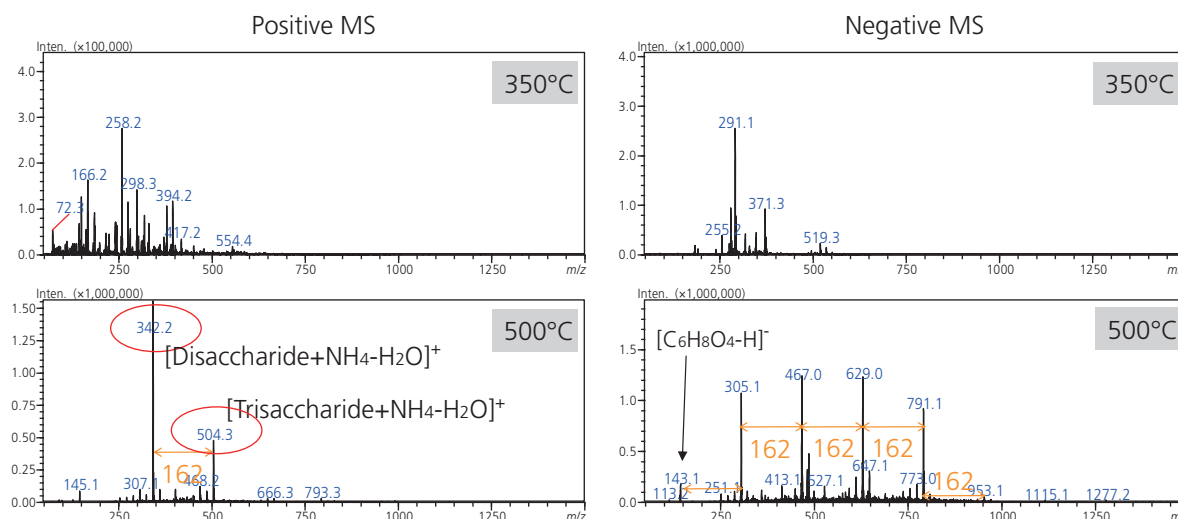


Fig. 4 DART gas heater temperature comparison; 350°C, 500°C mass spectra in positive/negative ion mode of starch

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3-2. Liquefied biomass

Next, liquefied biomass samples were analyzed. The liquefaction of starch in the presence of glycerol with sulfuric acid as a catalyst was conducted. Fig. 5 shows mass spectra of liquefied biomass. Abundant signals at m/z 269 and 343 in negative ion mode were observed. It was determined that these signals could be assigned to

$[\text{Glucose} + \text{C}_3\text{H}_6\text{O}_3 - \text{H}]^+$, $[\text{Glucose} + \text{C}_3\text{H}_6\text{O}_3 + \text{Glycerol} - \text{H}_2\text{O} - \text{H}]^+$. Signals m/z 297 and 371 were assigned to $[\text{Glucose} + \text{C}_5\text{H}_{10}\text{O}_3 - \text{H}]^+$, $[\text{Glucose} + \text{C}_5\text{H}_{10}\text{O}_3 + \text{Glycerol} - \text{H}_2\text{O} - \text{H}]^+$. This indicates that decomposition products of starch and Glycerol joined together during dehydration synthesis.

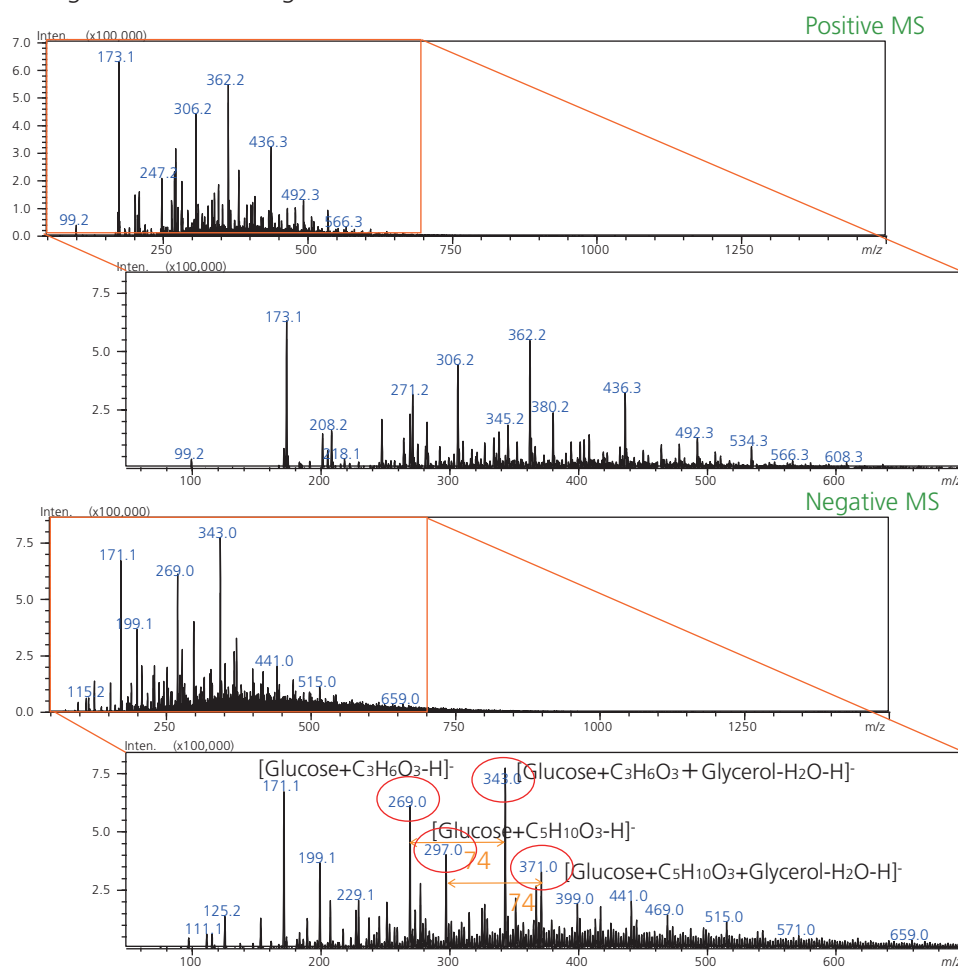


Fig. 5 Mass spectra in positive/negative ion mode of Liquefied Biomass

3-3. Biopolyol and its polyurethane foam

A biopolyol and its polyurethane foam and reagents were analyzed. A biopolyol biomass/plastics composite was made from liquefied biomass and propylene oxide, which could decrease the hydroxyl number and viscosity of the product and increase reactivity with polyisocyanates. Polyurethane foams were derived from the biopolyol and foaming agents (H_2O). Analysis of the biopolyol and foam showed widely

distributed peaks ranging from low to high mass. In the spectrum of biopolyol, a characteristic mass interval of 58u was observed in both polarities (Fig. 6). However, this characteristic mass interval of 58 u was not found in liquefied starch analysis. The mass interval of 58u probably corresponds to the propylene oxide ($\text{C}_3\text{H}_6\text{O}_3$). This shows that propylene oxides graft copolymerize to liquefied starch.

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The lower the viscosity of biopolyol, the more 58 u interval signals in mass spectra were observed. It suggested that the amount of PO addition related to the viscosities of

biopolyols. One reason may be that the addition of PO weakens hydrogen bonds among the liquefied starch molecules.

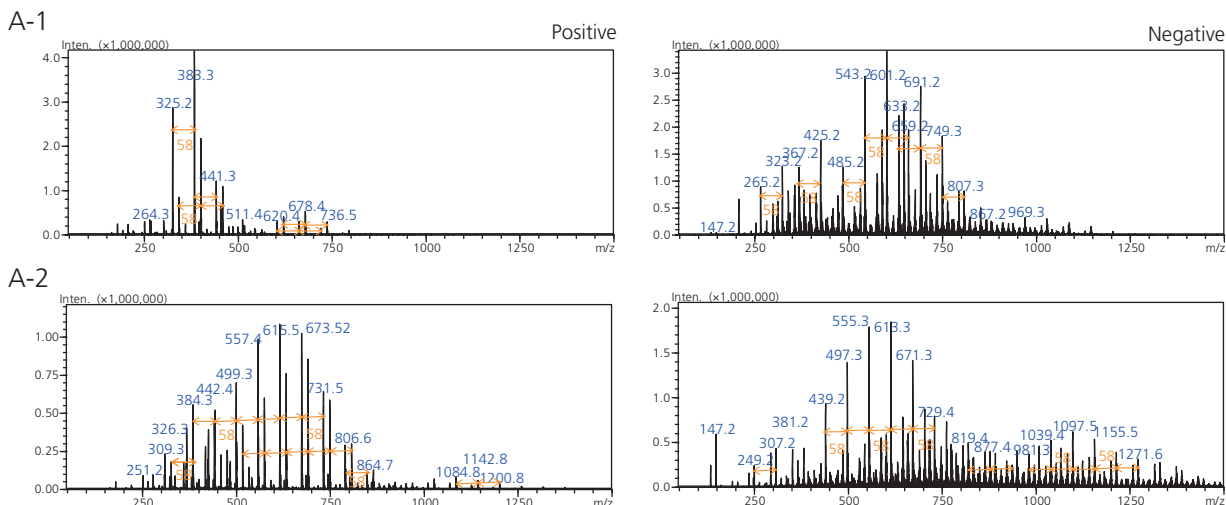


Fig. 6 Mass spectra in positive/negative ion mode of biopolyols

Table 2 Hydroxyl values and Viscosities of Biopolyols

	A-1	A-2
Hydroxyl value (mgKOH/g ⁻¹)	568	270
Viscosity (mPa · s)	5,699	837

A-400 is a polyurethane foam made from the mixture of biopolyol A -1 and A-2. The same signal interval was also observed in the spectrum of foam made from biopolyol (Fig. 7). Furthermore, common peaks were found between

foam A-400 and biopolyol A-1, A-2. This shows that foam made from biopolyol retains the chemical structure of biopolyol including the propylene oxide graft.

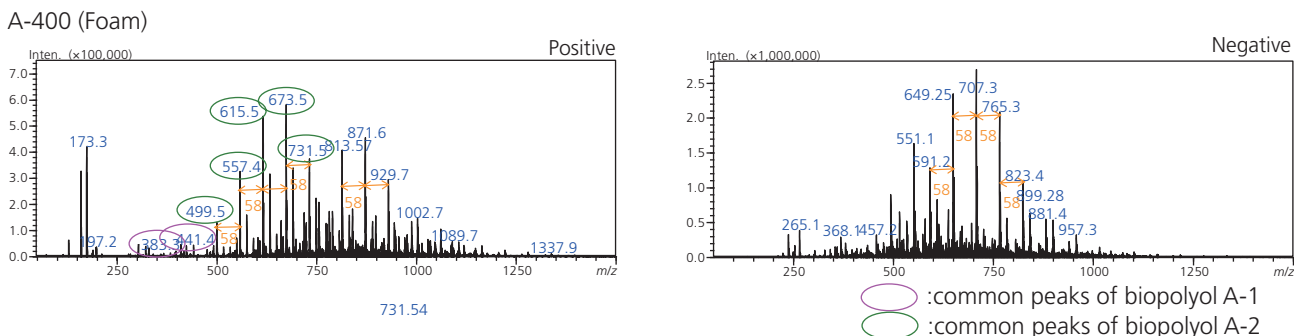


Fig. 7 Mass spectra in positive/negative ion mode of foam made from biopolyol

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4. Conclusions

- Ultra-fast polarity switching is useful for DART analysis of biopolyol (Propylene Oxide (PO) –added liquefied starch) and DART is capable of analyzing biopolyol with no sample preparation.
- Characteristic chemical structures of biopolyol were successfully determined.