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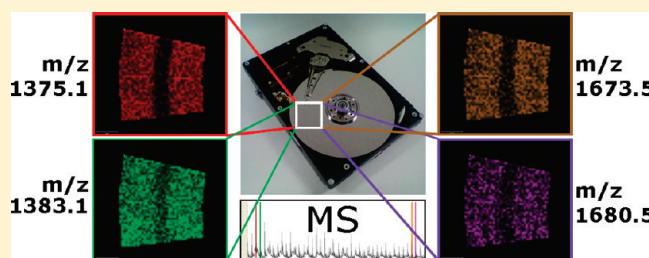
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ABSTRACT: Modern life is dependent on computer technology, and because the volume of digital data in the world is increasing rapidly, the importance of data storage devices is also increasing rapidly. Among them, demands for magnetic disk drive well-known as hard disk drives is quite huge and information recording density on the disk media is continuing to grow dramatically. For the research and development of the magnetic disk media, it is critical to investigate and characterize the lubricant layer formed on the disk media surface. However, it is difficult because the layer is only a monolayer which has only approximately 1 nm thickness in many cases. Although matrix-assisted laser desorption ionization-time-of-flight-mass spectrometry (MALDI-TOF-MS) measurements of monolayers have already been reported (Su, J.; Mrksich, M. *Langmuir*, **2003**, *19*, 4867–4870), lubricants used here are (co)polymers which have molecular weight distributions and are mixtures of various degrees of polymerization. This can reduce the sensitivity of MS measurement because the number (or density) of distinct single molecular species is lower than for homogeneous samples. In this report, direct measurement and characterization of lubricant monolayers using the LDI-TOF-MS instrument is performed to gain insight into detailed information like average molecular weight, polymer distribution, and two-dimensional mapping directly from magnetic disk monolayers. To our knowledge, this is the first time such information was acquired directly from hard disk media. The technique reported here might open up new possibilities also for investigations of various electronic devices other than magnetic hard disks.



In a magnetic disk drive, disk medium is spinning at high speed (e.g., 5400 or 7200 rpm). Storage and retrieval of magnetic signals are done by a magnetic head floating closely over the disk medium surface. Since it is necessary to narrow the gap between disk medium surface and head for high density signal recording, current devices generally have the gap below 10 nm and even sub-1 nm gaps were achieved in experimental study.^{1,2} Therefore, for reliability and durability of the devices, disk media have a layer structure consisting of a protection layer and a lubricant layer on the magnetic recording layer which are required to be as thin as possible for high density recording. Actually the lubricant layer of devices currently available on market seems to be a monolayer of perfluoro-polyether (PFPE) having approximately 1 nm thickness.^{1,3,4} On the other hand, a reduced floating height of magnetic head can result in trouble because of degradation of the lubricant layer caused by the contact of disk medium surface and head and a following molecular structure change of the lubricant or the transfer of lubricant molecules to the head. The direct monitoring of the lubricant layer on disk media as well as improvements of lubricant molecules itself will become quite important for high recording density, high performance, and high reliability of magnetic disk drives. However, detailed analysis of lubricant layers was difficult because of its low thickness. There are some

measurement techniques available to acquire information directly from disk media surface, but their information is not comprehensive, e.g., FT-IR⁴ cannot acquire single molecular information but only average information from sample mixtures or time-of-flight-secondary ion mass spectrometry (TOF-SIMS)^{5,6} cannot acquire molecular ion information but only fragmented ion information.

(Matrix-assisted) laser desorption ionization ((MA)LDI)-TOF-MS instruments are widely used for the analysis of biopolymers like peptides or proteins^{7–9} and well-known for its high sensitivity. The versatility of (MA)LDI-TOF-MS is continuously expanding to, e.g., identification of microorganisms^{10,11} or biomarker discovery^{12,13} and other applications. While most of traditional mass spectrometers are generally able to analyze samples in solution only, (MA)LDI-TOF-MS can also deal with solid samples by direct laser irradiation. It is possible to create two-dimensional image mappings from solid sample surfaces. This is known as imaging MS or MALDI imaging.^{14–17} In some cases, imaging MS without MALDI matrix addition can be performed if the target molecules are amenable to ionization only with laser

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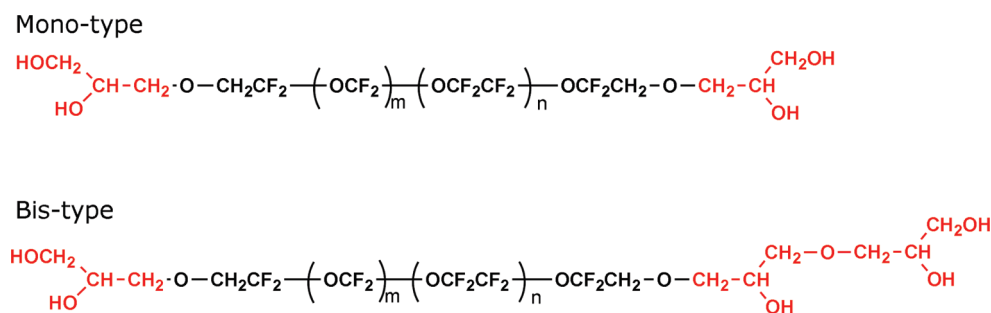


Figure 1. Structure of PFPE used in this study. There are two types of end groups, monotype (top) and bistype (bottom). From the combination of OCF_2 and OCF_2CF_2 monomer unit masses, the MS signal interval which should be observed is 16 Da both in the cases of the mono- and bistype. On the other hand, the mass difference between the mono- and bistype, which is caused by a mass difference of the end groups, is 8 Da. Therefore, they can be distinguished by their absolute mass even if they are mixed, e.g., signals at m/z 1375, 1391, 1407... are derived from the monotype and m/z 1383, 1399, 1415... from the bistype.

irradiation.^{18–20} Further, the (MA)LDI process can ionize various synthetic polymers,^{21–24} and its soft ionization is expected to yield average molecular weight information without ion fragmentation often observed in TOF-SIMS measurements which are also used for disk media analysis. Thus, in this study direct analyses of disk media, lubricant layers by LDI-TOF-MS were attempted with insertion of disk media samples into the instrument. Since this is the first trial of direct measurement of magnetic disk media by LDI-TOF-MS, fundamental experiments like the optimization of measurement parameters or comparison between disk media samples and ordinary PFPE solution samples were necessary.

EXPERIMENTAL SECTION

An autoflex III TOF/TOF LDI-TOF-MS instrument (Bruker Daltonics, Bremen, Germany) equipped with smartbeam laser was used for mass analysis. The Smartbeam laser has a special beam shape which is dynamically modulated and can acquire high signal intensity from small amount samples.²⁵ All spectra in this report were measured in positive reflectron mode. Acceleration and reflectron voltages were 19 and 21 kV, respectively. Instrument control and basic data handling was performed with flexControl and flexAnalysis 3.3 software. Imaging MS measurements were done using flexImaging 2.1 software. For polymer analysis like average molecular weight and end group composition calculations, Polymerix 2.0 software (Sierra Analytics, CA) was used. Polymerix can deal with copolymer as well as homopolymers and several end-groups simultaneously.

Samples. PFPEs used in this report were “Fomblin Z-Tetraol” purchased from Solvay Solexis (Italy) and consist of monotype and bistype end-group species (Figure 1). Solvent used for PFPE solution samples was Vertrel XF from Dupont-Mitsui Fluorochemicals Company, Ltd. (Tokyo, Japan), and the typical PFPE concentration was 200 ppm. A PFPE lubricant layer was formed on disk media samples (2.5 in. disk, typically less than 1 mm thickness, from Fuji Electric Device Technology Co., Ltd., Yamanashi, Japan) by the dip method in which disk media are dipped into the PFPE solution described above. After the disk media samples were withdrawn from the solution, the solvent was evaporated quickly and PFPE remains and forms a layer on the disk media surface. The layer thickness of PFPE lubricant was evaluated using C–F absorbance intensity from FT-IR measurements and was typically 1.2 nm. This thickness is indicating that the lubricant layer could be monolayers.¹

Sample Preparation for Mass Spectrometry. Solution samples were mixed with sodium trifluoroacetate (NaTFA, from TCI, Tokyo, Japan) solution (1 mg/mL in THF) by a ratio of 20:1 and applied onto a ground steel target plate. No MALDI matrix was used. As for disk media samples, NaTFA solution (0.2 mg/mL in THF/HFIP = 1:1) was sprayed on the disk surface with an airbrush device (Procon Boy FWA, GSI creos, Tokyo, Japan). THF (tetrahydrofuran) and HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) were purchased from Merck (Darmstadt, Germany) and Aldrich (MO), respectively. After spray preparation, the disk samples were fixed on a Prespotted AnchorChip (PAC, Bruker Daltonics, Germany) frame with electrically conductive double sided tape for SEM (Nisshin EM, Tokyo, Japan). Inherently, the PAC frame is an adapter for disposable targets, and since it has an approximately 1 mm deep surface recess, it is possible to fix and insert up to 2.5 in. sized disk media into the MS instrument (Figure 2). Generally, MALDI-TOF-MS target plates must have electric conductivity to avoid charging on the surface which would lead to signal broadening and signal intensity decrease. This is the reason why conductive carbon tape is used and typical electrical resistance between the PAC frame and disk media sample surface was below a few hundred kilohms.

RESULTS AND DISCUSSION

Fundamental Experiment A: Addition of Salt onto Disk Media Samples. Figure 3 shows a comparison between spectra of the PFPE lubricant layer on the disk medium surface with and without salt addition by spray. MALDI matrix was not used because preliminary experiments showed that matrix addition seemed to decrease the sensitivity of PFPE signals. Although there is a study which is reporting fluorinated matrix to be suitable for PFPE²⁰ in the past, less matrix amount leads to better spectra and it is possible to measure it even without matrix. This tendency seems to be more prominent when the sample amount is smaller, and the matrix is still effective when the sample is abundant. Therefore, in the cases of the small sample amounts handled in this report, surface effects of target plates or disk media might be considered like NALDI^{26,27} target plates or other matrix-free target plates.²⁸ The exact principle of the ionization mechanism on these surfaces is still unclear, but their concepts seem to be based on a kind of DIOS plate originally reported in ref 29. Comparison between two surfaces (disk medium and normal MALDI target plate), thus comparison between solution and disk samples, will be discussed in the next section,

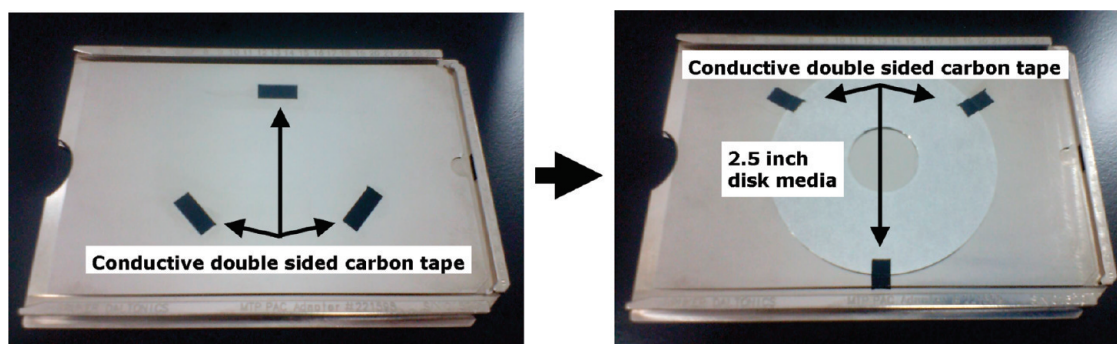


Figure 2. PAC frame to insert disk medium samples into the LDI-TOF-MS instrument. The carbon tapes under the disk media are used as an adhesive, and the ones on the disk media are used to ensure electric conductivity between the PAC frame and disk medium surface. Since this disk medium has electric conductivity between two sides, electric conductivity between the disk medium and PAC frame is obtained at six positions in total.

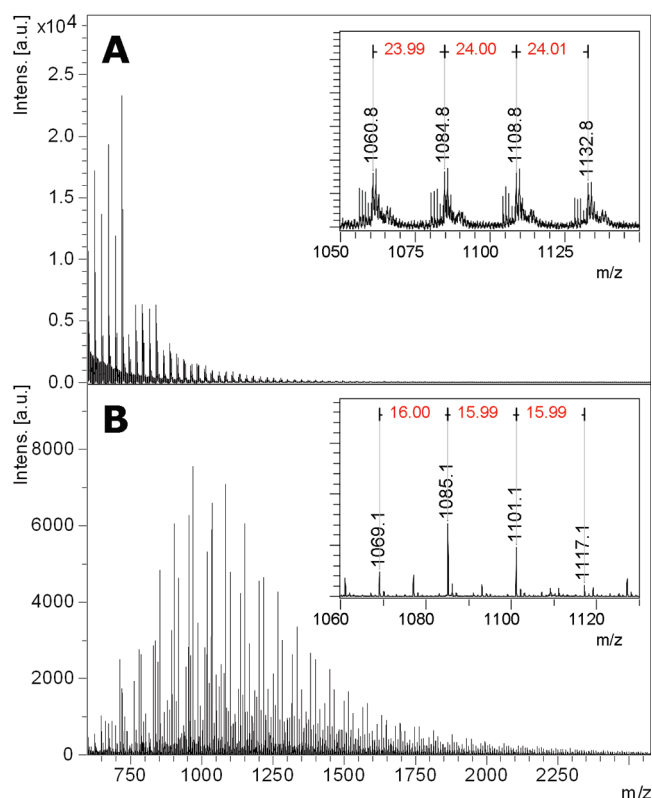


Figure 3. MS spectra of PFPE lubricant layers on disk media measured without (A) NaTFA and with (B) addition by air-brush spray preparation. Although both spectra were recorded from same disk medium, part A was from a naked, untreated area and part B was from an area coated with NaTFA. Inserts in the figure are zooms of the respective spectra showing different mass intervals. The signals with interval of m/z 24 are considered to be carbon clusters originating from the carbon protection layer of disk media, while the interval of m/z 16 originates from PFPE, which is also supported by the observation of similar molecular weight distributions.

Fundamental Experiment B: Comparison between Solution and Disk Medium Samples. Salt addition turned out to be necessary, and PFPE could only be measured under the presence of sodium (or other salts) and gave rise to signals with $m/z = 16$ intervals. Without sodium addition, mass intervals of $m/z = 24$ were observed and considered to be carbon cluster peaks caused from

carbon used as the protection layer under the lubricant layer or from analyte degradation. Because the addition of sodium is sufficient at very small amounts, relatively good measurements might be possible without a spray coating but also due to sodium or potassium contaminations from the atmosphere depending on the environment of experiments or the history of the disk media. However, active addition is desired for certain measurements to limit the cation species attached and thus reduce sample complexity. Lithium or silver ion addition yields respective adduct signals, and their comparison might be helpful to confirm the cation species attached to the molecule observed in the spectra.

Fundamental Experiment B: Comparison between Solution and Disk Medium Samples. Figure 4 shows a comparison between PFPE solution samples measured from a normal target plate (ground steel) like ordinary MALDI measurements and the PFPE lubricant layer on disk media applied by dipping disks into the solution. Two types of PFPE (A and B) and their mixture were used here. Since PFPE A and B have different mono/bis ratios, their mixture samples have also different mono/bis ratios depending on the mixing ratio. Signals are relatively intense in solution sample spectra rather than disk medium sample spectra. Although some errors can exist, almost the same average molecular weight values were calculated both from solution, and disk media samples showing consistent measurements can be done directly from polymer monolayers on disk media. Here, number and weight average molecular weight and mono/bis ratio were all calculated using Polymerix. In both cases of solution samples and disk media samples, bis-type is ionized with higher efficiency and saturated already at a mixture rate of 79:21. At each mixing ratio, bis signals seem to be observed intensely in particular from disk medium samples. This will be discussed in the next section, Experiment 1: PFPE Composition Change with Continuous Disk Media Dipping. Despite that LDI-TOF-MS is generally said to be unsuitable for (absolute) quantitative analysis, this stable result shows the possibility for relative quantitation using this method, which is desirable in combination with other types of analyses such as TOF-SIMS.

Experiment 1: PFPE Composition Change with Continuous Disk Media Dipping. In a production process, a lot of disk media is dipped into the same PFPE solution. The composition of PFPE solution is known to change and degrade after a while. Figure 5A shows the bis ratio against the mono calculated from mass spectra of PFPE solution samples and disk media samples picked from an actual production line. Sample no. 1 was taken right after fresh solution preparation, and sample no. 2 was taken

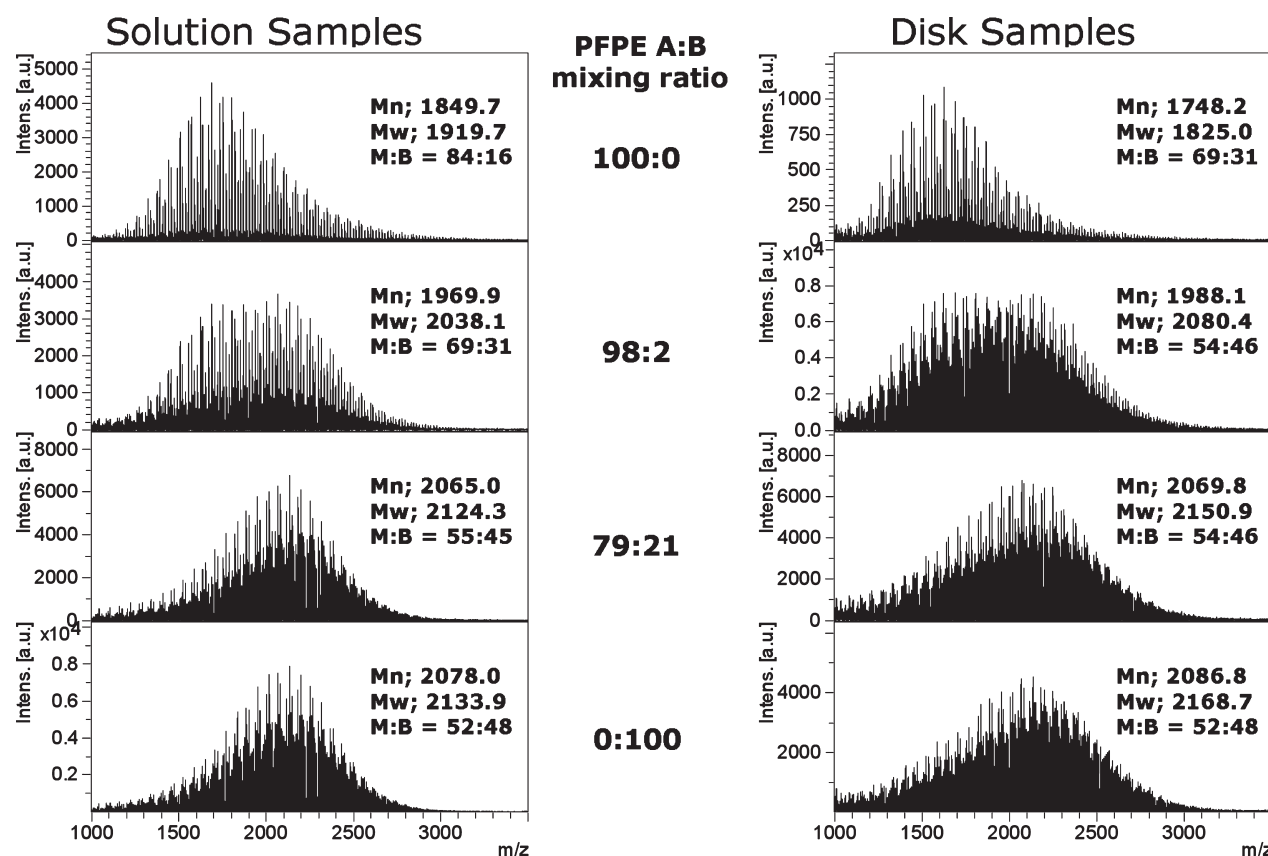


Figure 4. PFPE samples with various mixing ratios measured as solution samples (on standard target plate) and lubricant layers on disk media samples. In the figure, Mn means number average molecular weight, Mw means weight average molecular weight, and M:B means mono/bis abundance ratio calculated from mass signals. Relatively good agreement between solution samples and disk medium samples is showing the reasonableness of this method to evaluate lubricant layers directly from disk medium samples.

after mass production of disk media. The bis ratio at sample no. 2 is reduced in both solution and disk media samples, and this is more prominent in solution samples. Further on, in every case, disk media samples show a higher bis ratio than solution samples, indicating that bis-type has a tendency to be adsorbed easier onto disk media surface, when this is dipped into the solution.

This could be caused by the number of hydroxyl groups which have higher reactivity and affinity with the disk surface.³ Bis-type, which has more hydroxyl groups in its molecular structure than the monotype, could be adsorbed onto disk media surface with higher efficiency. This effect might be possible to be analyzed also with TOF-SIMS using fragment ion mass signals including end groups. However, with MALDI-TOF-MS, not only the bis/mono ratio but also average molecular weight information can be obtained (Figure 5B). No significant change was observed between sample numbers 1 and 2. According to this, the major parameter determining adsorption tendency is assumed not to be the molecular weight but the end groups. To our knowledge, this is the first time for direct measurement and acquisition of such information ever.

To reduce the production cost of disk media, multiple usage of PFPE solution is quite important. To ensure long time performance, readdition of components reduced in concentration during usage by adsorption is necessary. Sample no. 3 is the one in which the components are adjusted after drawing of sample no. 2, and sample no. 4 corresponds to sample no. 3 after a further (second) round of mass production. The result of

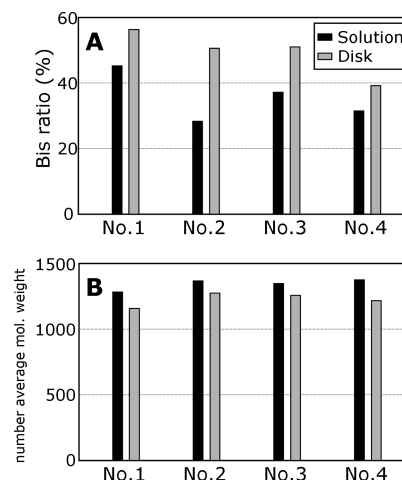


Figure 5. Calculated values from PFPE solution and disk medium samples from actual disk medium production line. The bis against mono ratio is shown in part A, and the number average molecular weight is shown in part B. Sample no. 1 is from freshly prepared solution/disk medium. Sample no. 2 is after mass production of disk media. The PFPE component of sample no. 3 was adjusted after drawing of sample no. 2 for further production. Sample no. 4 corresponds to no. 3 after further (second) mass production.

sample no. 3 is relatively close to the one of no.1 but not exactly identical. Adjustment of the components was done so far according

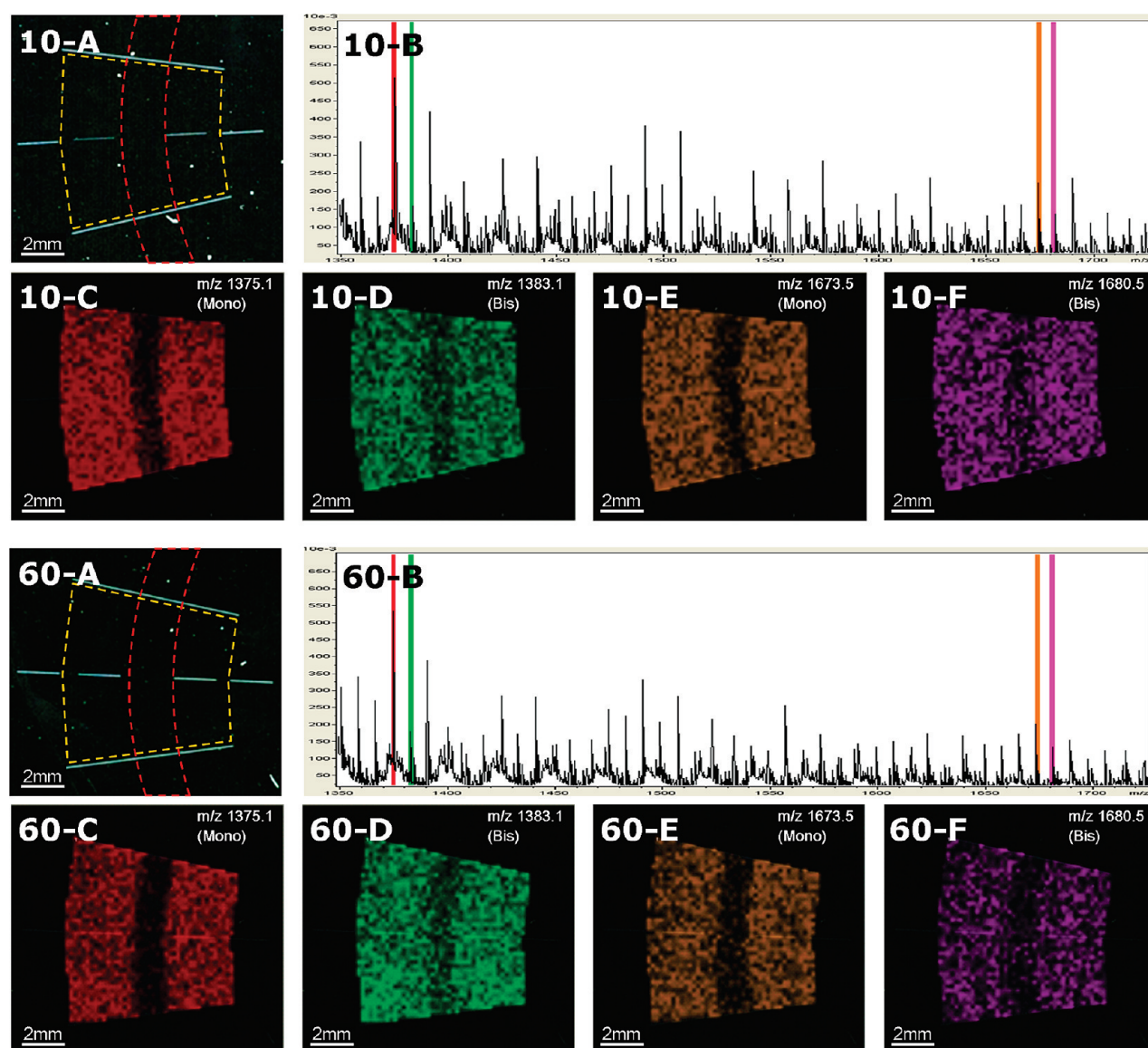


Figure 6. Imaging MS results of disk medium samples after the lube wear test. Numbers of 10 and 60 in the figure show the duration of the test in minutes. Part A is a photograph of a part of a disk medium taken by an office scanner. Thin white lines in part A are markings on the media surface, and red broken lines show the tested (degraded) region, while yellow broken lines show the imaging MS measurement region. Part B is the average spectrum of all acquired spectra from the measuring region. Parts C–F show signal intensity image as color density. Part C (red) stands for m/z 1375.1 which is the one of the mono signals. Part D (green) stands for m/z 1383.1 (Bis), Part E (yellow) stands for m/z 1673.5 (mono), and part F (purple) stands for m/z 1680.5 (bis), respectively. Reduced color intensity indicates reduced analyte concentrations in worn media areas.

to a rule of thumb in the factory, but these results indicate that this is not sufficient and performance can be improved by exact monitoring of the individual analyte concentrations. The relationship between sample numbers 3 and 4 seems to be different from the one between samples numbers 1 and 2. This study does not cover the detailed reasons of these differences, but of course some differences of the components like, e.g., their relative amount, should cause it. Such information would be helpful for the accurate adjustment of the solution components and also for study of the relationship between solution components and adsorption onto the disk medium surface.

Experiment 2: Evaluation of the Lube Wear Test. It is known that the lubricant layer of the disk media degrades after long time usage. Two possibilities can be considered as the reason for this: (1) decrease of the molecular amount of the

lubricant by material transfer to the magnetic head or (2) change of the lubricant's molecular structure. Both can be caused by the physical contact between the disk medium surface and the magnetic head. It is possible to imprint the wear pattern (degraded area) on a disk medium surface in a short time by scribing with the magnetic head under a low-pressure environment and with high-speed disk rotation. Figure 6 shows the imaging MS result of disk media sample on which the wear pattern was added under the condition of 10 000 rpm, 425 hPa, 2 mm width, and two durations (10 and 60 min). The imaging MS measurement was done with a spatial resolution of 200 μm . A total of 300 laser shots were irradiated per spectrum, and around 1500 spectra were recorded per sample in total. Visualization of molecular weight is done with maximum signal intensity within the $\pm 0.05\%$ region of m/z 1375.1, 1383.1, 1673.5, and 1681.5,

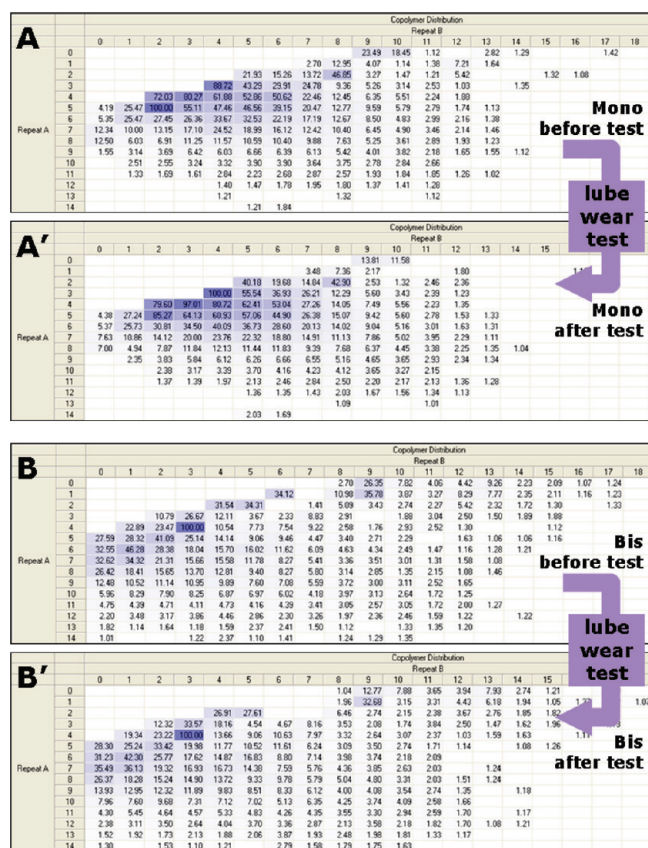


Figure 7. Distribution of CF_2O and $\text{C}_2\text{F}_4\text{O}$ monomer units investigated from mass spectra of the sample after the lube wear test for 60 minutes. Part A shows the distribution concerning mono species, whereas part B refers to the bis species, respectively. Parts A and B without an apostrophe correspond to the data from outside the area of (i.e., before) the lube wear test. Parts A' and B' correspond to the data from inside the test area after the lube wear test. The X axis represents the number of CF_2O unit contained in observed species in the spectra, and the Y axis represents the number of $\text{C}_2\text{F}_4\text{O}$ units. The values in the columns indicate relative abundance with a color code. The higher value corresponds to deeper color (purple). Since it is relative abundance, the maximum value is always 100.00. The figure shows that the general distribution before and after the lubricant wear test is almost identical.

which correspond to mono, bis, mono, and bis species, respectively, as indicated in the figure. Although the tested region cannot be recognized by the naked eye (Figure 6 10 and 60 A, scan image by an office scanner, GT-X750, Epson, Nagano, Japan), the imaging MS can visualize it with reduced signal intensities both of mono and bis species. In comparison between the 10 min test and 60 min test, the latter shows relatively clearly the contrast between inside and outside of the test region, indicating that MS signal intensities are gradually decreased with increasing test duration. Furthermore, images of monotype species indicate a clearer contrast than the bis-type species. This can be caused by higher intensities (therefore less effect from noise) of mono species as well as by the reasons discussed in the following paragraph.

The Polymerix software was used for detailed analysis of the spectra, and three results were obtained. (1) The number average molecular weight before the test (outside the tested region) is 1296 and after the test (inside the tested region) is 1276. The weight average molecular weight before the test is 1389 and after the test is 1366 (these calculations are including both mono and

bis species and are averaged values of two measurements). Thus, average molecular weight is not changed much after performing the test. This shows that the degradation of the lubricant is not depending on its molecular weight. (2) Figure 7 shows that there is almost no difference in the distribution of CF_2O and $\text{C}_2\text{F}_4\text{O}$ monomer units between before and after the test. This shows that the degradation of lubricant is not dependent on its monomer unit distribution, i.e., molecular structure of polymer backbone. (3) Mono/bis signal intensity ratio found to be changed after the lube wear test. Mono/bis before the test is 2.57 and after the test is 2.03. This shows that the amount of mono species decreases faster than that of the bis species in the test. This seems to be reasonable considering the stronger affinity of the bis species to the disk media surface in comparison to the mono species. From above, of the three results, the end-group structure or number of hydroxyl groups is considered to have the strongest effect on the disk media characteristics, and molecular weight or molecular structure of the polymer backbone seem to be of lower importance. In other words, the end-group structure has a stronger effect than physical size or length of polymer molecules and other characteristics directly related to them. This is in good agreement with the result of experiment 1. This study shows that the end group structure is very important both for disk production and disk degradation.

CONCLUSIONS

In the presented study, direct measurement of PFPE monolayers on magnetic disk media using an LDI-TOF-MS instrument was demonstrated by acquiring detailed information like average molecular weight, end-group composition, and monomer unit distribution. These are pieces of information which cannot be directly acquired from real magnetic disk media with any other method such as FT-IR, TOF-SIMS, NMR, or size-exclusion chromatography. Spectra acquired directly from disk media samples are consistent with those from solution samples measured using conventional MALDI target plates and measurement conditions. The most important point is that direct measurement is possible, and this is of great importance for the industry in which direct and detailed analysis of real products is difficult but nevertheless necessary for quality control or fault analysis. Further, imaging MS measurement could detect and visualize the differences between before and after the lube wear test of the disk media. The results show new information with regard to the average molecular weight, end-group composition, and monomer unit distribution and also show that the degradation of lubricants is not affected by its molecular size but almost exclusively by the number of hydroxyl group in the molecules. In most cases, samples investigated by imaging MS are biological tissue slices nowadays. However, the results obtained here are indicating that imaging MS is applicable also for industrial materials and can be a strong technique to acquire important information which cannot be acquired by any other method. Although this study is aimed at magnetic disk media, MALDI-TOF-MS, which has enough sensitivity even for copolymer monolayer analysis, is expected to expand its possibilities to other electronic devices.

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