Applications note
Polymer note

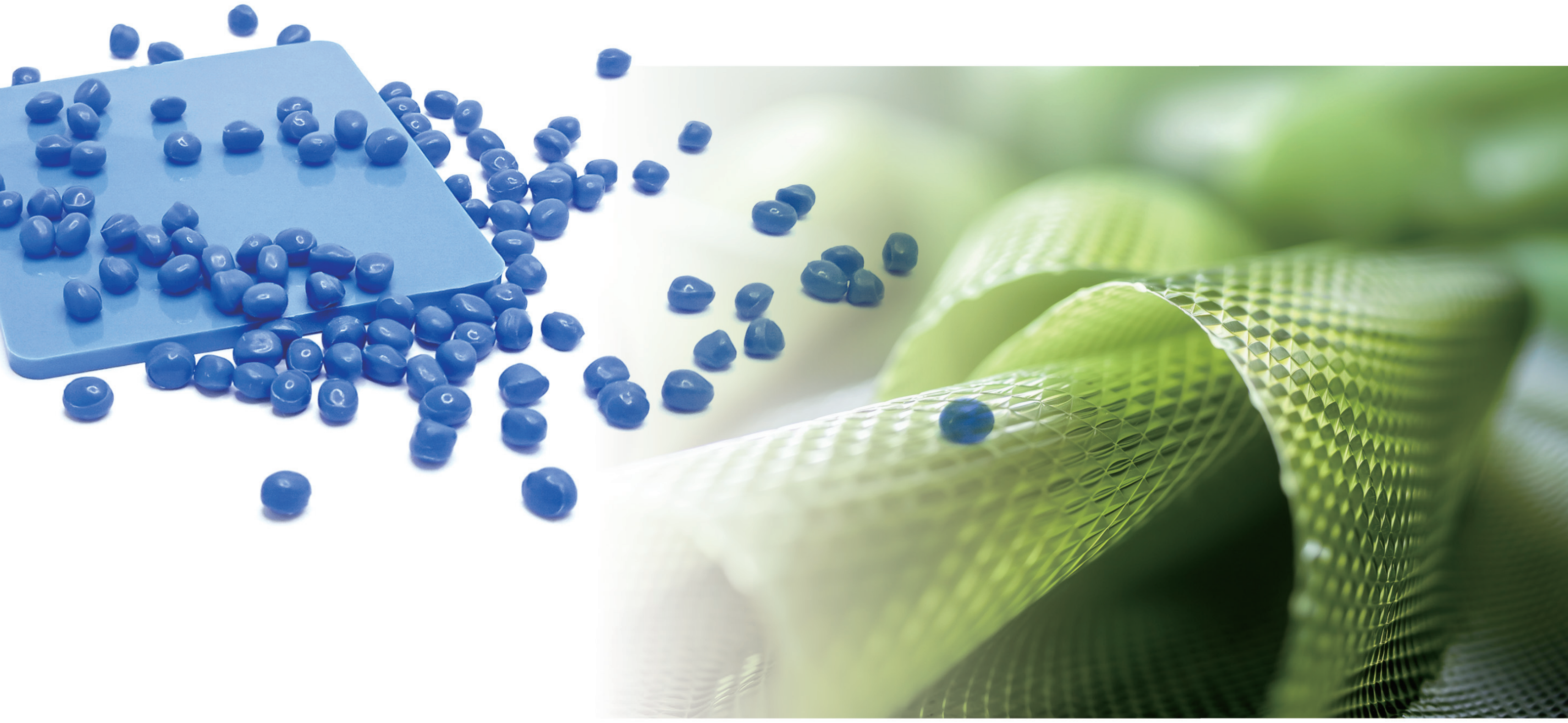
Solutions for Innovation

Polymer note

Chemical Analysis Instruments
NMR / ESR / MS / GC-QMS / GC-TOFMS / DART™-TOFMS / MALDI-TOFMS

Surface Analysis & Morphological Observation Instruments
XRF / XPS / SEM / TEM

YOKOGUSHI Applications·Analysis of Polyethylene Terephthalate



JEOL Ltd.

Polymernote

Characterization of Polymers by JEOL Solutions

Polymers are used in a wide range of fields such as food wrapping materials, medicine packing, and industrial materials and products. Properties and functionalities of polymer materials are dependent on various factors, including molecular weight, molecular weight distribution, molecular chemical structures (primary structures), morphology of molecular chains (secondary structures) depending on the spinning angles of chemical bonds, and crystalline or non-crystalline structures of inner-molecules and inter-molecules, as well as spherulite structure aggregates, phase separation structures and orientations (higher-order structures).
It is of prime importance to analyze and evaluate the structures and properties of polymers as well as the correlation between these two factors, and to feed these analysis and evaluation results to the development and manufacturing sites for the enhancement of the performance and quality control of polymer materials and polymer products. On the other hand, industry in Japan is supported by functional molecules, which are becoming more advanced and more complicated. This makes it more difficult to characterize such polymers, thereby increasing the importance of multiple analyses that combine a variety of analytical methods. This Polymer note introduces a broad range of instruments used for polymer analysis and their applications.

INDEX

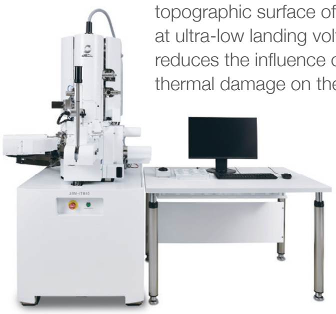
1. Main Analytical Instruments

Chemical Analysis Instruments

Surface Analysis & Morphological Observation Instruments

Polymer Analysis Technologies

FE-SEM enables observation of the top-surface structure and fine topographic surface of the specimen at ultra-low landing voltage, which reduces the influence of charging and thermal damage on the specimen.



Field-emission Scanning Electron Microscope (FE-SEM)

Transmission Electron Microscope (TEM)

By using the freezing method, TEM enables observation of the native structure of water containing specimens such as paints, adhesives, and cosmetics.
Thin-section specimens can be used for observing internal fine structures. Electron staining also enables observation of crystalline and non-crystalline structures and analysis of the mixture of blended polymers.

In addition to searching the library database using the EI method, accurate mass measurements using multiple ionization methods enables the analysis of components not registered in the library database.

Gas Chromatograph Mass Spectrometer (GC-MS)

Morphological Observation

Chemical Structure Analysis

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometer (MALDI-TOFMS)

MALDI Spiral-TOFMS enables the analysis of chemical structural information (including molecular weight, terminal structures, and copolymerization composition), average molecular weight, molecular weight distribution, copolymerization composition distribution, etc.

Chemical Analysis

Nuclear Magnetic Resonance (NMR)

NMR enables the analysis of chemical states (e.g. the molecular structures of solution and solid samples) and is capable of identifying differences between crystalline and non-crystalline states.

Surface & Interface Analysis

Elemental Analysis

X-ray Fluorescence Spectrometer (XRF)

XRF enables the average composition analysis of liquid, powder, and solid specimens, standard-less quantitative analysis (simple quantification), and non-destructive qualitative and quantitative analysis of additives and residual catalysts in synthetic polymers.

X-ray Photoelectron Spectroscopy (XPS)

XPS enables the analysis of composition and chemical bonding states at the top surface of a substance, as well as depth profile analysis of thin film samples in combination with ion sputtering.

Electron Spin Resonance (ESR)

ESR enables the analysis of the radicals formed in polymers. The targets are radicals derived from polymerization initiators and additives, growing radicals, and radicals formed during degradation.

Analysis of Various Polymer Materials

Monomer

Polymerization →

Polymer

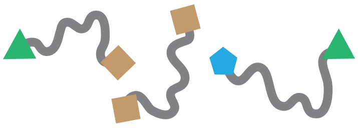
Molecular characterization

○ **Molecular weight and molecular weight distribution**

(Number-average molecular weight, weight-average molecular weight, etc.)

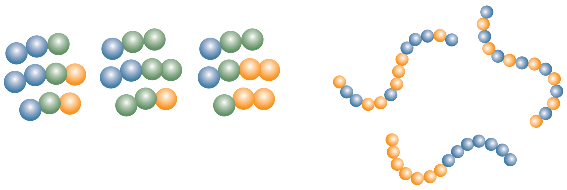
○ **Molecular structure**

(End group structure, etc.)



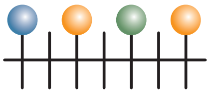
○ **Copolymer structure**

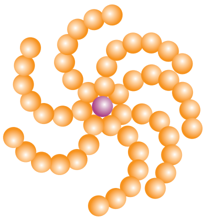
(Average chemical composition, Copolymer composition, chain structure, etc.)



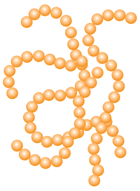
○ **Fine structure**

(Branching structure, stereo

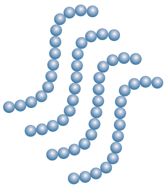




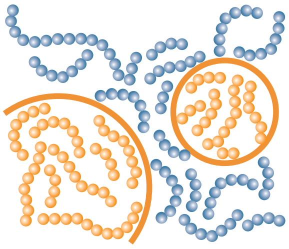
Amorphous polymer



Crystalline polymer



Blend polymer
(phase-separated structure)

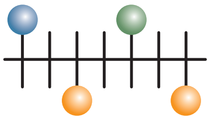


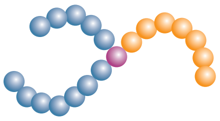
- Additives
- Other polymers

Molding material
Polymer products

Material characterization

-regularity, bonding mode, etc.)





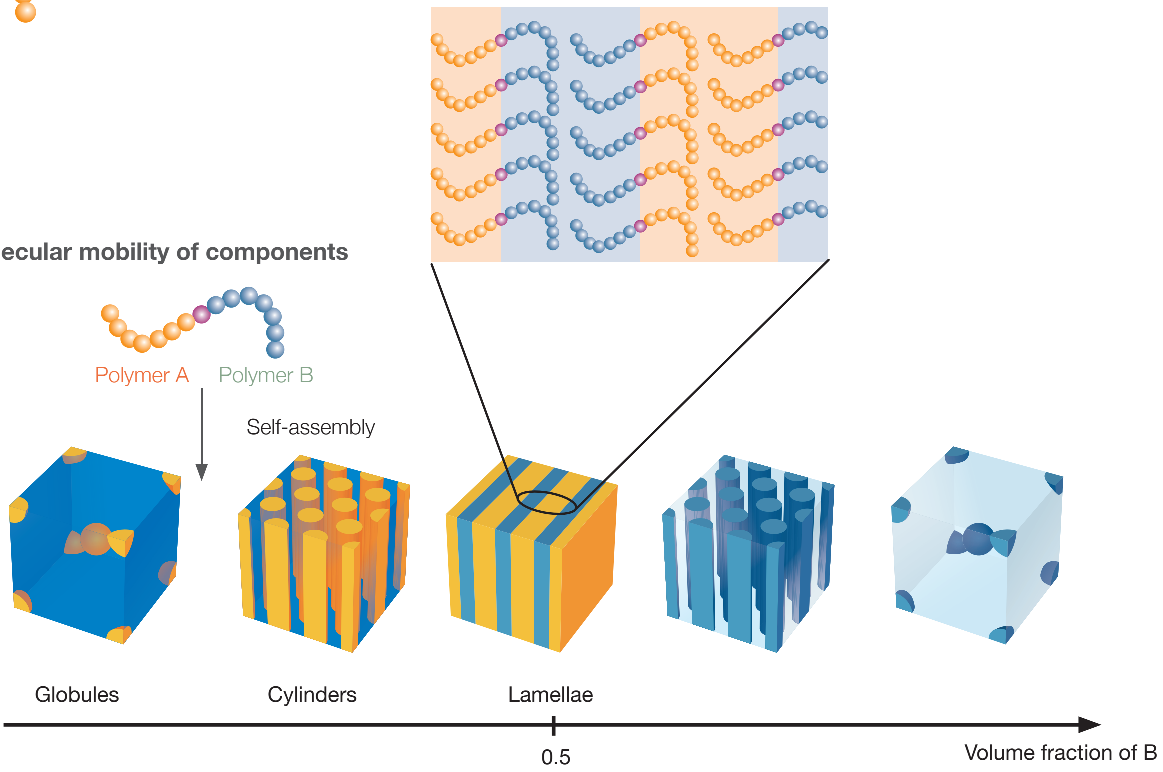
○ **Analysis of higher order structure**

(Crystal structure, orientation, Blend dispersed state)

○ **Surface, interface and local area analysis**

(Repellency, adhesion, foreign material analysis, chemical states, etc.)

○ **Molecular mobility of components**



1-1 Nuclear Magnetic Resonance System

NMR

The Nuclear Magnetic Resonance (NMR) System is an instrument that is used for obtaining data that relates the local chemical environment of a nucleus by irradiating a sample with radio waves while it is placed in a static magnetic field. As each nucleus in a polymer can have a different chemical environment due to factors such as molecular structures and crystalline structures, the observed peak positions (chemical shift values) will vary depending on the surrounding environment. NMR has a large number of applications for both solution and solid samples because it is capable of obtaining a wide range of chemical data including molecular structures, crystalline structures, quantification data and molecular mobility through non-destructive analysis methods.

NMR

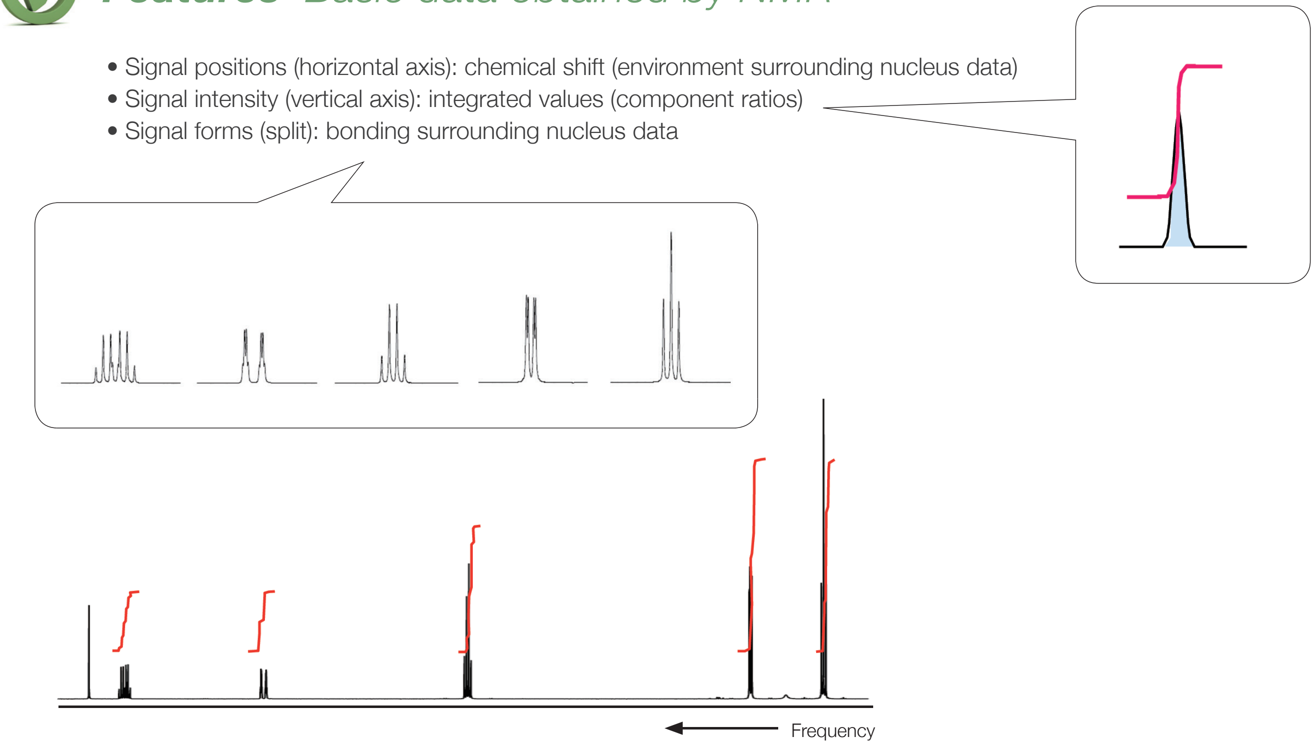
Non-destructive analysis
Enables analysis without destroying samples.

Structural analysis
Enables molecular structural analysis and crystalline structural analysis.

Quantitative analysis
Enables quantitative analysis of each component from the peak intensity.

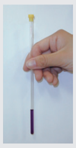
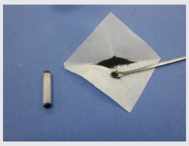
Features Basic data obtained by NMR

- Signal positions (horizontal axis): chemical shift (environment surrounding nucleus data)
- Signal intensity (vertical axis): integrated values (component ratios)
- Signal forms (split): bonding surrounding nucleus data



Features *Solution NMR and Solid-State NMR*

There are two types of NMR: solution NMR, in which the sample is dissolved in a solvent and measured, and solid-state NMR, in which the solid sample is measured as is.
The superconducting magnet and spectrometer are the same, but the shape of the detector (probe) and sample tube are different.
The method used to obtain the information varies depending on the purpose.

	Solution NMR	Solid-state NMR
Measurement	Dissolve the sample in solvent Glass sample tube 	Measure the sample as is Ceramic sample tube 
Sample	· Liquid sample · Solid sample soluble in solvents	· Sample that deteriorates when dissolved · Insoluble or poorly soluble in solvents · A solid with an unknown structure
Main probe (detector)	5 mm ROYALPROBE™ GR probe	3.2 mm AUTOMAS probe
Information obtained	Molecular structure Tacticity Chained information Physical properties in solution	Solid structure (Crystal polymorphism, crystallinity, amorphous analysis, etc.) Molecular compatibility (polymer-polymer, polymer-additive) Physical property analysis in solid state (mobility)

Useful Probes and Peripherals for Polymer Measurements

Pre-heating auto sample changer

NMR measurements of polymers often require high-temperature measurements. The JNM-ECZ series improves the efficiency of continuous measurement of multiple samples by raising the temperature in advance with the pre-heating automatic sample changer for solution NMR. In solid-state NMR, continuous measurements are possible by the top-loading type AUTOMAS probe corresponding to high temperatures. JEOL's auto sample changer is applicable to both solid-state and solution samples.

*Note: Preheating of solid samples is not supported.

Room temperature 30-tube slot
(Samples in the heating slot are also collected in the room-temperature slot after measurement)

Room-temperature 12-tube slot

Models used: JNM-ECZ500R, Pre-Heat ASC30

ROYALPROBE™ AUTOMAS

Use of the ROYALPROBE™ AUTOMAS enables solid-state NMR measurement with the same usability as solution NMR

- Loading and unloading the sample tube with the auto sample changer and ROTORCARRIER™
- Tuning
- Adjusting the magic angle

All of the above can be performed automatically. In addition, it can measure temperature change from -100 °C to 220 °C, making it ideal for analysis of polymers that require a wide range of temperature variations.

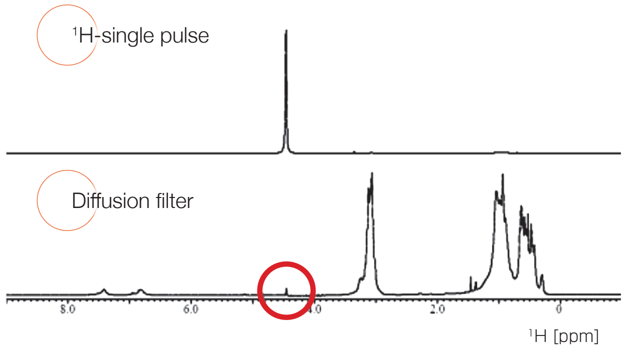
ROYALPROBE™ AUTOMAS

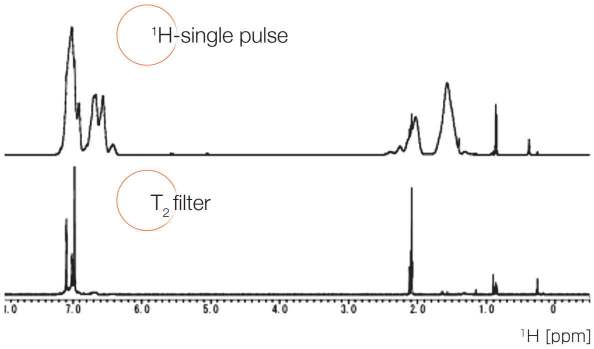
ROTORCARRIER™

https://www.jeol.com/solutions/applications/details/NM180007.php

Applications Mixture analysis

Solution NMR enables the analysis of not only single-component samples but also the individual components of composite samples with a mix of low and high weight molecules (without the need for fractionation).



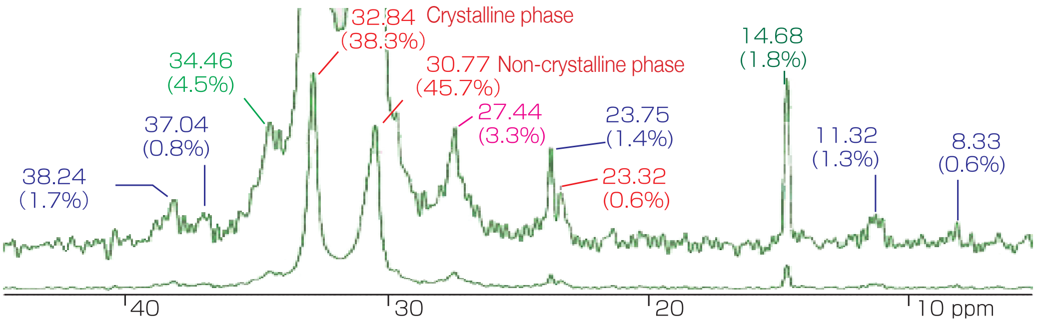


Sample: detergent (neat)
Top: ^{1}H-NMR spectrum
Bottom: Selective acquisition of polymer components
Signals of water were excluded to analyze components of overlapping peaks.

Sample: Styrofoam (heavy-toluene solution)
Top: ^{1}H-NMR spectrum
Bottom: Selective acquisition of low-molecular components
Polymer components were excluded and data of only low molecular weight components are obtained.

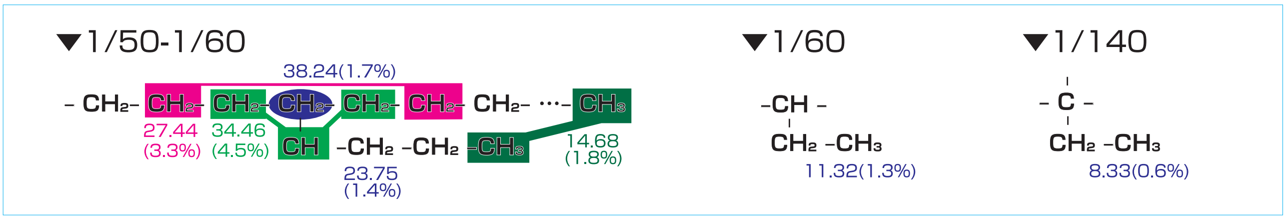
【Reference】JEOL Application Note: NM130004, NM130005

Applications Quantitative analysis of polyethylene – solid-state NMR -



In solid-state NMR, the CPMAS method, which has good sensitivity, is commonly used, but its weakness is that it is not quantitative; measurements under quantitative conditions using the DDMAS method can provide insight into the degree of crystallinity and the molecular weight of insoluble polymers.

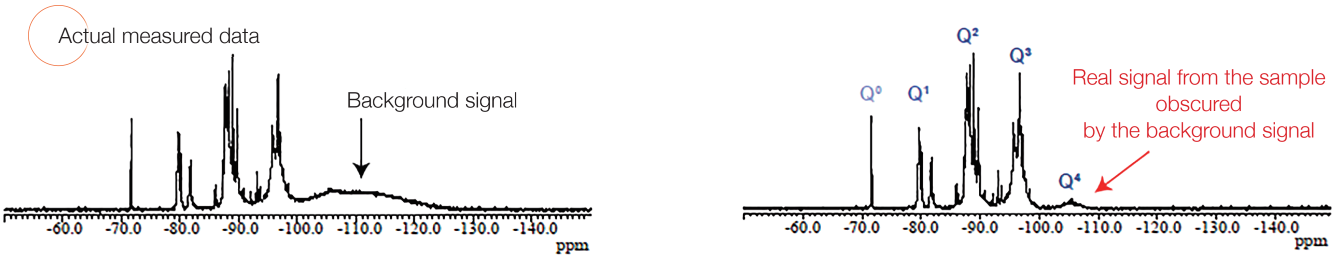
- 46% degree of crystallinity was obtained from the ratio between the CH_2 peak of the crystalline phase observed at 32.84 ppm (intensity ratio: 38.3%) and the non-crystalline phase CH_2 peak observed at 30.77 ppm (intensity ratio: 45.7%).
- An estimate of the branching ratio was made from the peak intensity ratio of other terminal components.



【Reference】JEOL Application Note: NM130011E

Applications Structural Analysis of Silicon Polymers - Solution NMR-

NMR is used to analyze silicon polymers and water glass, which are becoming more widely used. In solution NMR, the background signal from the probe was an obstacle to the analysis of the Q4 structure. However, in recent years, the silicon background has been removed from many probes. The analysis of silicon polymers has become easier.

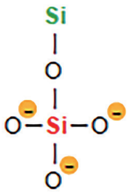


Sample: Sodium silicate solution/D2O
Spectrometer: JNM-ECAII600

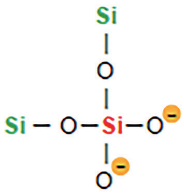
Left spectrum: Obtained using a 10 mm tunable probe and heat-resistant glass tube
Right spectrum: Obtained using a 10 mm ^{29}Si probe and fluororesin tube

Particularly effective for broad peaks with a low signal-to-noise ratio (S/N)

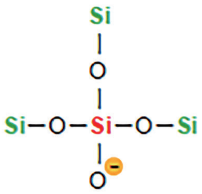
Q^1 : O×4、O-Si×1



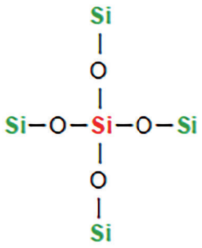
Q^2 : O×4、O-Si×2



Q^3 : O×4、O-Si×3



Q^4 : O×4、O-Si×4



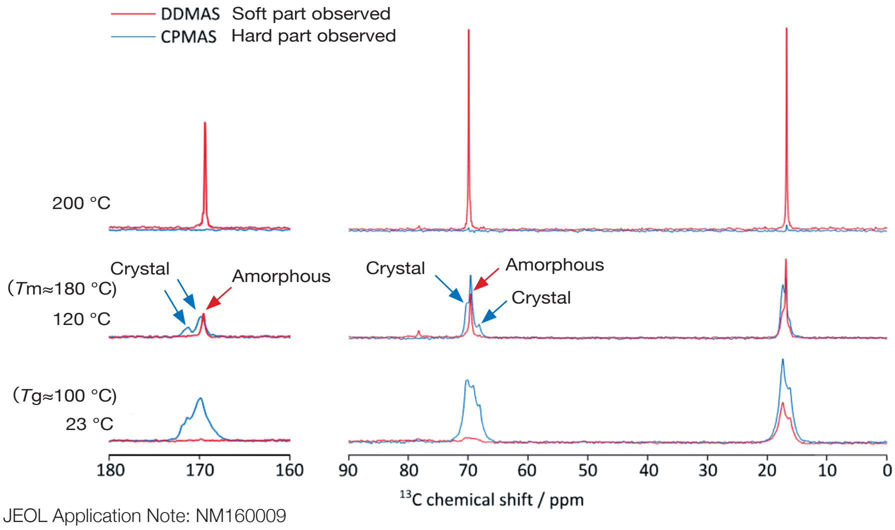
【Reference】 JEOL Application Note: NM130006E
https://www.jeol.com/solutions/applications/details/NM130006E.php

Applications Analysis of Phase Transition in Crystalline Polymers - Solid-state NMR-

Almost all crystalline polymers are mixed materials of crystalline and amorphous parts. In addition, the mobility of molecules, which plays a major role in physical properties, changes in a complex manner at the glass transition temperature (T_g) and the melting temperature (T_m) of the crystal. By using CPMAS and DDMAS, which are basic measurements methods of solid-state NMR, it is possible to selectively observe the hard and soft parts of the polymer chain, making it possible to identify the signals of crystalline and amorphous parts and analyze the mobility of the polymer chain.

For DDMAS measurements, the repetition time was set to a relatively short time (2 seconds), to highlight areas with a short ^{13}C relaxation time (high mobility).

At or below the glass transition temperature T_g, the signal of the amorphous part appears only in CPMAS because the mobility of both the crystalline part and the amorphous part is low. In contrast, above the T_g, the mobility of the amorphous part increases, so the signal of the amorphous part appears in the DDMAS spectra. When the crystal melts (above T_m), the CPMAS spectrum does not appear, but the signal with a thin line width in a molten state is observed in DDMAS.



【Reference】 JEOL Application Note: NM160009

1-2 Electron Spin Resonance

ESR

ESR is a magnetic resonance instrument that operates on the same principle as NMR. While NMR observes the nuclear spins of the sample and records the spectrum in the absorption waveform, ESR selectively observes only the electron spins of the unpaired electrons in the sample and records them in the first derivative waveform. It is much more sensitive than NMR.

Radical reactions are involved in the synthesis process, thermal degradation, and photoaging of polymers. Many of the reactions of polymerization inhibitors, antioxidants, and light absorbers used to control them are also considered to be radical-mediated. These reactions can be observed using ESR.

Observation can be performed by sweeping the magnetic field while irradiating microwaves of a certain frequency

Any sample, solids, liquids, or gases, can be observed in a cell of 4 mm in inner diameter without any pretreatment

Non-destructive detection of radicals in the entire sample

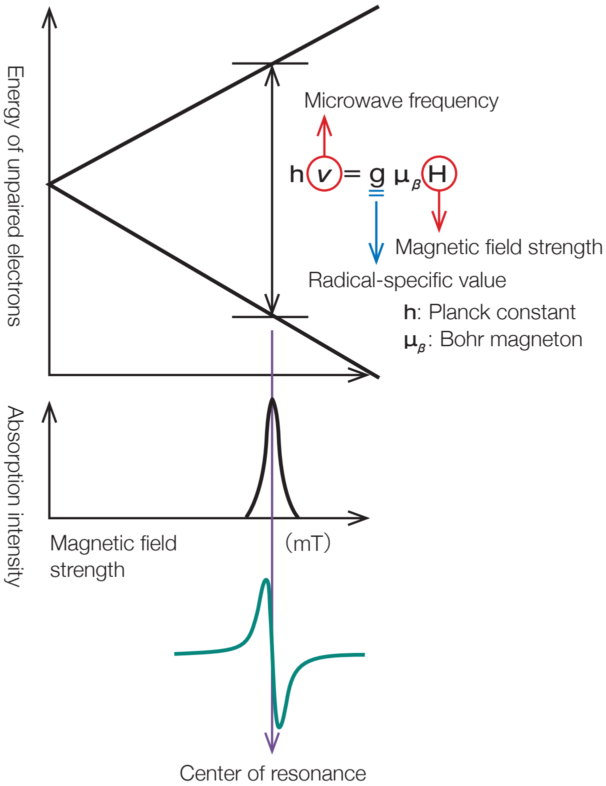
Radical species can be identified from signal position and waveform, and quantitative analysis can be performed from signal intensity

Principle

The electron spins of unpaired electrons split into two energy orders in a magnetic field. When microwaves with energy equivalent to this splitting energy are irradiated, microwave absorption occurs in the resonating magnetic field. The ESR spectrum is recorded as a higher-resolution derivative waveform.

The g value of the resonance equation shown on the right figure is a radical-specific value and is an important factor for identification.

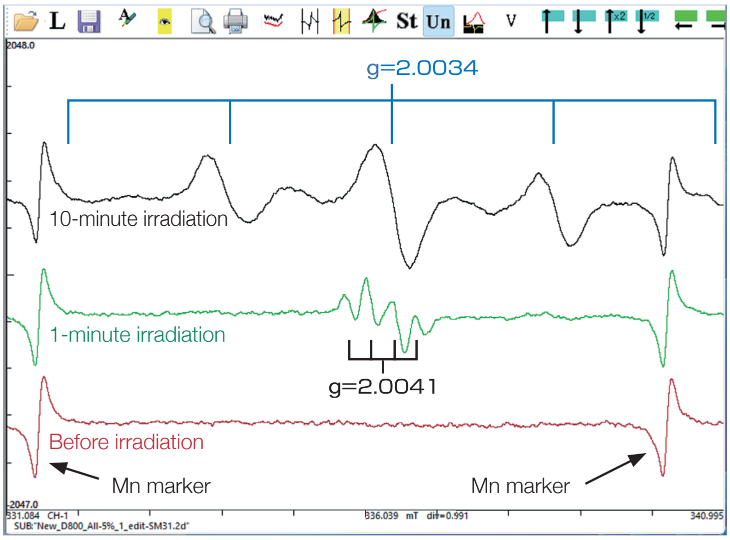
The nuclear spin of the atoms around the radicals in the molecule causes the signal to split in some cases, which makes it possible to analyze the structure of the radicals.



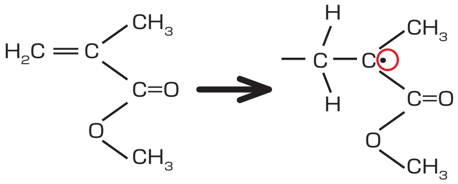
Applications Initial Radical Formation by Light Irradiation of Light-Curing Resin

The embedding agent for an electron microscope was collected in a liquid state in an ESR sample tube, and the in-situ measurement was performed while irradiating the light of a mercury-xenon lamp. The result is shown in the figure below.

Bottom: Before irradiation, middle: 1-minute irradiation, top: 10-minute irradiation



No radicals were detected before irradiation, but four lines giving g = 2.0041 were observed at the initial stage of irradiation. The signal decreased with subsequent irradiation, and the formation of five broad lines was observed instead. The latter was deduced from the g value and waveform as an acrylic acid radical, which is the main component.



Acrylic acid monomer

Acrylic acid radical

It was suggested that the initial radical was a phenol-based polymerization inhibitor because of the g-value commonly seen in phenoxy radicals and the time-dependent change of the main radicals after they disappeared.

In this way, the series of reaction between additive and monomer can be evaluated by ESR evaluation.

Applications Change of Radicals Due to Thermal Decomposition of High-Performance Resins

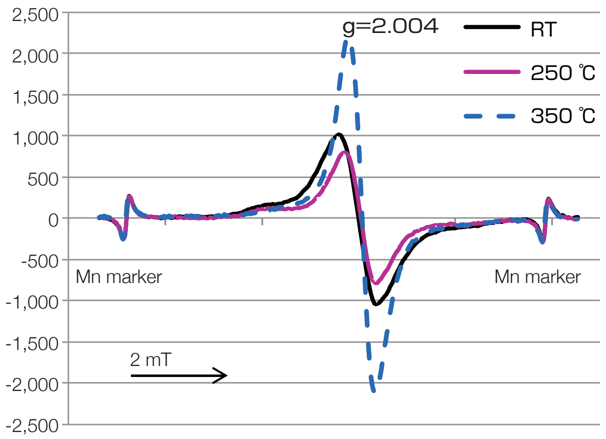
In recent years, the development of heat-resistant resins as high-performance resins has been progressing. Pyrolysis with radical formation is known as a thermal degradation mechanism of resins. In many cases, radicals are unstable, making it difficult to evaluate them in analytical methods that require manipulation such as separation and extraction from samples.

ESR has the advantage of selectively detecting radicals, so sample pretreatment is not required. This is an example of an in-situ measurement that applies high temperature on a commercially available polyamide-imide resin (PAI) sample by using an ES-13070VT400, variable temperature controller, which can heat up to 400 °C using air as a medium, to measure the radicals generated.

Sample: PAI resin (heat resistance temperature: 250 °C) molded into approximately 2 × 2 × 10 mm

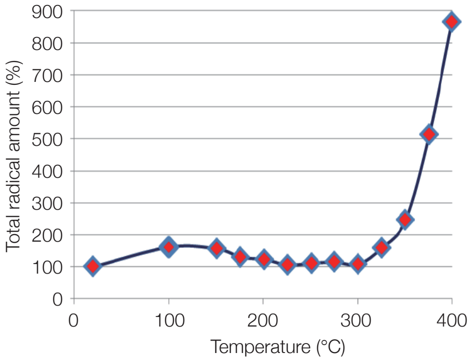
Measurement: At room temperature, 100 °C, then heated every 25 °C between 150 °C and 400 °C

The figure below shows the spectra obtained at room temperature, 250 °C and 350 °C.



A clear signal of g = 2.004 was observed even at room temperature, suggesting that unpolymerized radical molecules may still exist.

The total radical amount was determined from the spectrum at each temperature, and the temperature dependence was shown in the below graph with the amount at room temperature as 100%.



The amount of radicals rose during heating to 100 °C, then gradually decreased during heating to 300 °C, and started to increase at higher temperatures.

In this way, the change of radicals from low temperature to heat-resistant temperature is expected to provide important information for the thermal degradation of heat-resistant resins.

1-3 Mass Spectrometer: MS

GC-QMS / TOFMS

The Gas Chromatograph-Mass Spectrometer (GC-MS) is an instrument for molecular mass measurement of volatile compounds separated by gas chromatography. The Quadrupole Mass Spectrometer (QMS) is the most common mass spectrometer, which is used for various applications due to its compact size and versatility. Recently, the Time-of-Flight Mass Spectrometer (TOFMS) has also gained popularity for its higher resolution. Combined with various pretreatment units, GC-MS can analyze components in gas, liquid and solid samples.

Mixture separation

Separates vaporized components by gas chromatography. Analyzes separated gas components by MS.

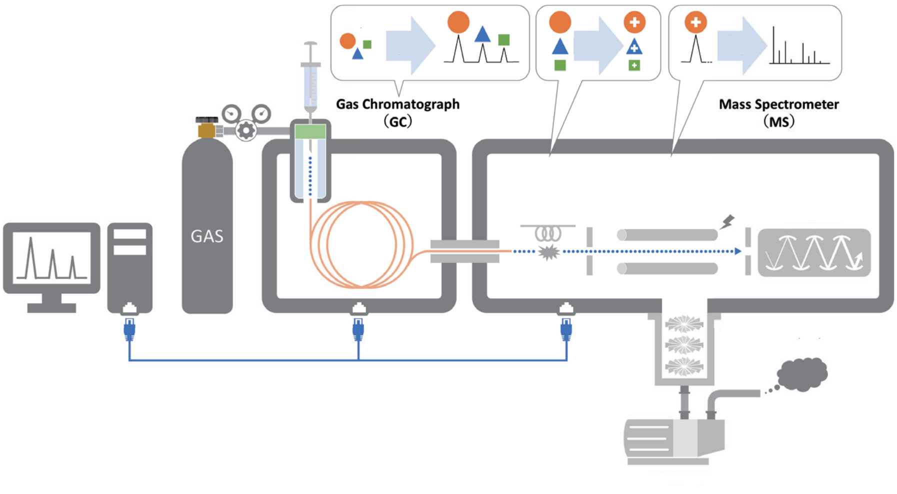
Identification of detected components

Identifies detected components by searching the database for the obtained EI mass spectrum. The composition formula of any detected ion is estimated by an accurate mass measurement. (For GC-TOFMS only)

Quantitative analysis

Performs quantitative analysis by comparing the ion intensities of the standard and actual samples.

Principle Gas Chromatograph-Mass Spectrometer (GC-MS)



Gas chromatograph:	Separates vaporized mixture components based on principles of partition chromatography. Separated components are sequentially introduced to the ion source of the mass spectrometer.
Ion source:	Ionizes components separated by the gas chromatograph. There are various methods of ionization, including electron ionization (EI).
Mass analyzer:	Separates and detects generated ions according to the mass-to-charge ratio (*m/z*). A mass spectrum can be obtained by using *m/z* as a horizontal axis and ion intensity as a vertical axis.

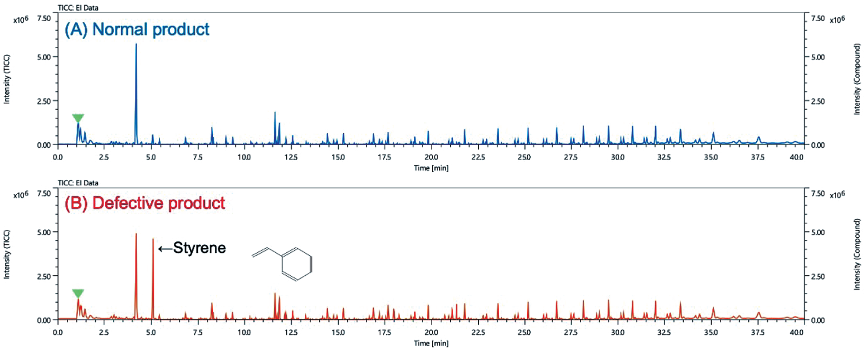
Applications Example of Analysis of Defective Resin by Pyrolysis-GC-TOFMS

The pyrolyzer system is a pretreatment instrument often used in the analysis of synthetic polymers. It is possible to analyze additives by thermal extraction and analyze polymers by pyrolysis.

The following is an analysis example of normal and defective polypropylene (PP) products by the pyrolysis-GC-TOFMS.

GC-TOFMS and the Frontier Laboratories Ltd. Multi-Shot Pyrolyzer EGA/PY-3030D

TICC: EI method



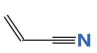
12 characteristic components were found in defective PP products. A structure analysis of the 12 components observed only in the defective products revealed that all of them had structures suggesting hybrid dimers and trimers of acrylonitrile styrene (AS) copolymer. From this, the foreign matter mixed into the defective product was identified as an AS copolymer.

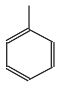
Analysis results of 12 components characteristically observed in defective products

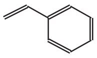
General				Total Result								
ID	RT [min]	Height [%]	IM m/z	Compound Name	Lib.	Similarity / AI Score	Formula	DBE	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage
003	1.27	4.83	53.02651	2-Propenenitrile	mainlib	778	C_3H_3N	3.0	53.02600	0.51	0.91	100
007	3.00	2.15	92.06214	Toluene	mainlib	921	C_7H_8	4.0	92.06205	0.09	0.89	100
012	5.09	65.31	104.06269	Styrene	mainlib	965	C_8H_8	5.0	104.06205	0.64	0.96	100
023	12.14	4.99	157.08970	2-methylidene-4-phenylbutanenitrile	AI	904	$C_{11}H_{11}N$	7.0	157.08860	1.09	0.94	100
026	13.25	3.54	157.08966	4-phenylpent-4-enenitrile	AI	855	$C_{11}H_{11}N$	7.0	157.08860	1.06	0.91	100
034	16.86	2.90	208.12615	3-phenylbut-3-enylbenzene	AI	833	$C_{16}H_{16}$	9.0	208.12465	1.50	0.86	100
040	17.68	2.80	210.11566	2-methylidene-4-(2-phenylethyl)pentanedinitrile	AI	729	$C_{14}H_{14}N_2$	9.0	210.11515	0.51	0.67	100
041	17.98	8.52	210.11544	2-methylidene-4-phenylheptanedinitrile	AI	622	$C_{14}H_{14}N_2$	9.0	210.11515	0.29	0.69	100
042	18.26	3.28	210.11623	2-(2-phenylprop-2-enyl)pentanedinitrile	AI	711	$C_{14}H_{14}N_2$	9.0	210.11515	1.08	0.88	92
046	20.70	3.63	261.15184	2-methylidene-4,6-diphenylhexanenitrile	AI	660	$C_{19}H_{19}N$	11.0	261.15120	0.64	0.72	100
048	21.09	3.93	261.15180	3,6-diphenylhept-6-enenitrile	AI	538	$C_{19}H_{19}N$	11.0	261.15120	0.60	0.80	100
050	21.33	9.43	261.15152	4-phenyl-2-(2-phenylethyl)pent-4-enenitrile	AI	597	$C_{19}H_{19}N$	11.0	261.15120	0.32	0.85	100

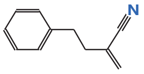
mainlib=NIST library, AI=AI structure analysis

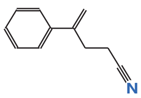
Estimated structural formulas of 12 components that were characteristically observed in defective products

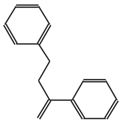

ID003
Acrylonitrile: A

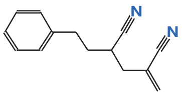

ID007
Toluene

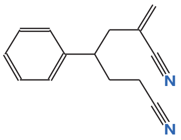

ID012
Styrene: S

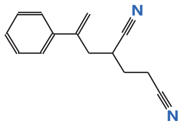

ID023
AS dimer

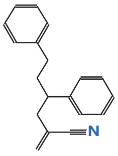

ID026
SA dimer

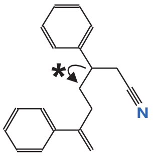

ID034
SS dimer

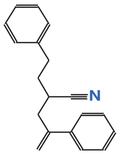

ID040
AAS trimer


ID041
ASA trimer


ID042
SAA trimer


ID046
ASS trimer


ID048
SSA trimer


ID050
SAS trimer

* Side chain position differs from literature

Mass Spectrometer: MS

DART™-TOFMS

DART (Direct Analysis in Real Time) is a newly-developed ionization method called "ambient ionization" that ionizes samples under atmospheric pressure. Using this method, samples of various forms and states can be ionized for mass spectrometry by TOFMS simply by exposing the sample to DART™ ion sources.

Fast measurement

Samples only need to be exposed to the ion source for seconds.

No sample preparation

Allows samples in various forms to be analyzed.


Liquid sample

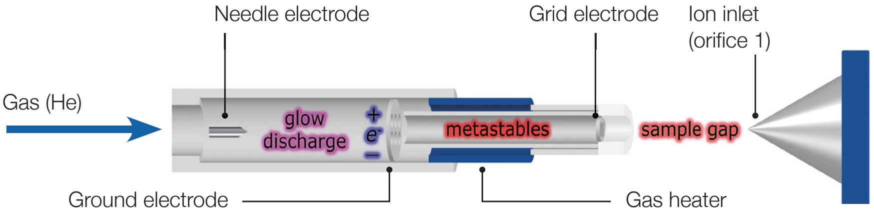

Solid sample


Powder sample

Qualitative analysis by accurate mass measurement

Composition formula of any detected ion is estimated by an accurate mass analysis.

Principle DART ionization



Schematic of DART™ ion source

< DART-positive mode >

$He (2^3S) + H_2O \rightarrow H_2O^{+\cdot} + He (1^1S) + e^-$

$H_2O^{+\cdot} + H_2O \rightarrow H_3O^+ + OH^\cdot$

$H_3O^+ + nH_2O \rightarrow [(H_2O)_{n+1} + H]^+$

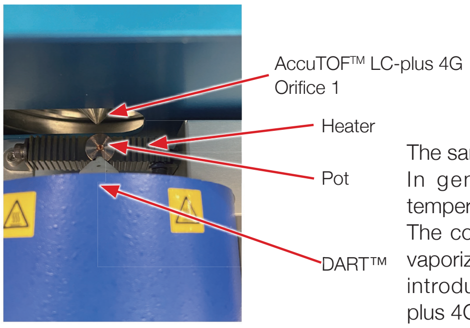
$[(H_2O)_{n+1} + H]^+ + M \rightarrow [M + H]^+ + (n+1) H_2O$

M: Sample molecules

Helium gas introduced to the DART™ ion source becomes excited helium atoms by means of a discharge from the needle electrode. Ionization progresses due to the interaction among excited helium atoms, atmospheric gases, and sample molecules.

Applications Resin Analysis by Thermal Desorption/Pyrolysis DART™

By combining it with a temperature-programmed heating device, resin analysis is possible using thermal desorption/pyrolysis (TDP)-DART™-TOFMS. Oligomers that have been cleaved once are observed in the initial stage of heating. The pyrolysis products, that have been cleaved once, contain information on the terminal groups.

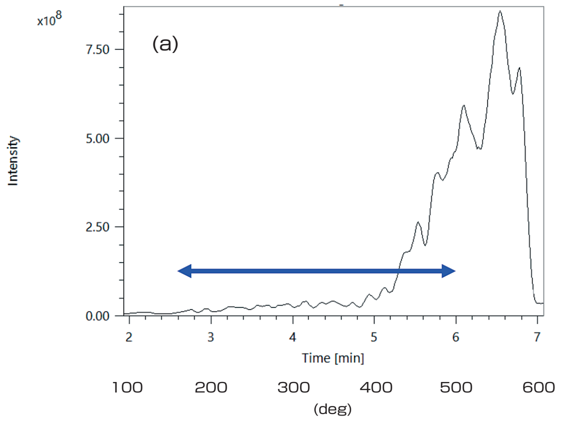


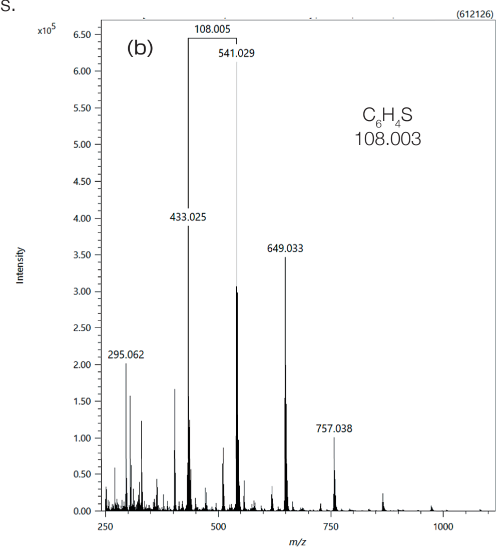
The sample is placed in the pot. In general, the heater raises the temperature linearly at 100 °C/min. The components that are heated and vaporized are ionized by DART™ and introduced into the AccuTOF™ LC-plus 4G.

Polystyrene sulfide (PPS) was analyzed by TDP-DART™-TOFMS and many polymer series with 108 u intervals were observed.

PPS analysis by TDP-DART™

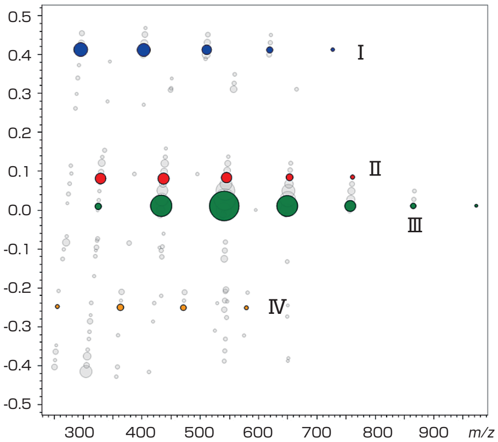
Figure a shows the change in the total ion intensity as the temperature rises.
Figure b shows mass spectrum between 150 and 500 °C.

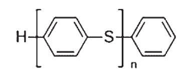
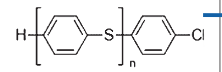
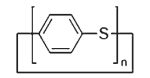
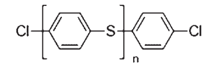




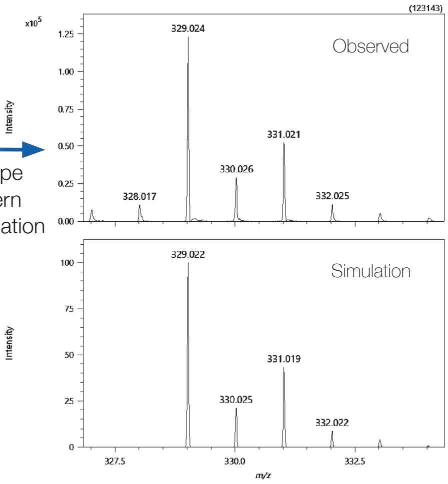
Kendrick mass defect (KMD) analysis

The KMD analysis of the mass spectrum obtained in the upper stage revealed four main series.
Series II and Series IV had terminal chlorophenyl groups.
These results suggest that this sample was synthesized by the Phillips method.



	Estimated structure
I	
II	
III	
IV	

Isotope pattern confirmation



Mass Spectrometer: MS

MALDI-TOFMS "SpiralTOF™-plus 3.0"

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometer (MALDI-TOFMS) is a mass spectrometer capable of analyzing substances ranging from low molecular weight compounds such as amino acids to high molecular weight compounds such as synthetic polymers. JMS-S3000 "SpiralTOF™-plus 3.0" is the highest-class resolution MALDI-TOFMS incorporating an ion optical system that has a proprietary spiral trajectory (SpiralTOF ion optical system).

MALDI-TOFMS "SpiralTOF™-plus 3.0"

Measurement of low- to high-molecular substances

Enables analysis of high molecular weight samples with tens of thousands of molecules using the linear TOF option.

Qualitative analysis by accurate mass measurement

Enables estimation of the composition formula of any detected ion by an accurate mass analysis.

TOF-TOF option for structural analysis

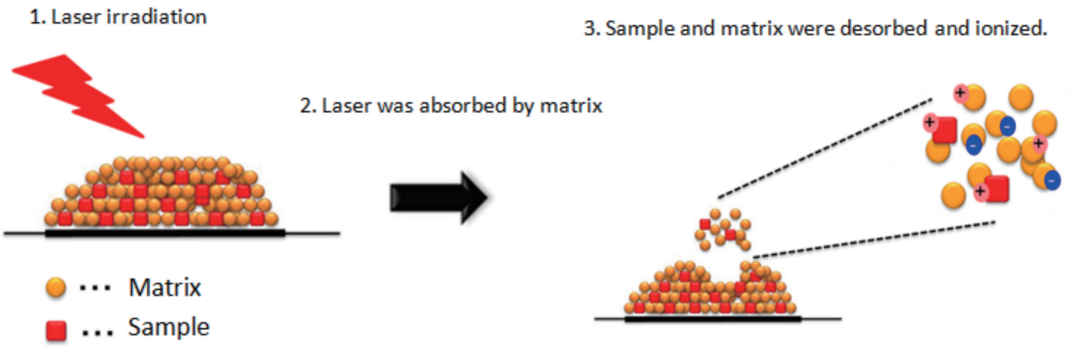
In the TOF-TOF analysis, only ions with an *m/z* value selected in the first-stage TOFMS are selected. Selected ions (precursor ions) are excited from a collision with an inert gas such as He, which causing ion bond cleavage and fragmentation (generating product ions). The structure data of organic compounds can be obtained from the spectrum of product ions analyzed by the second-stage TOFMS.

MS imaging analysis

Provides organic compound distribution data on the sample surface.

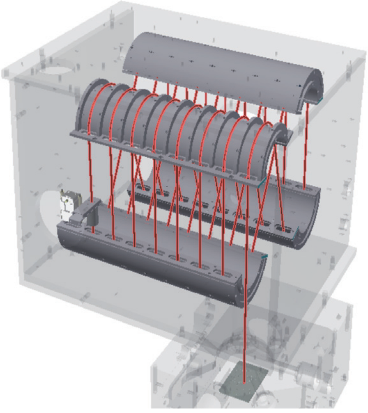
Principle Matrix-assisted laser desorption/ionization method

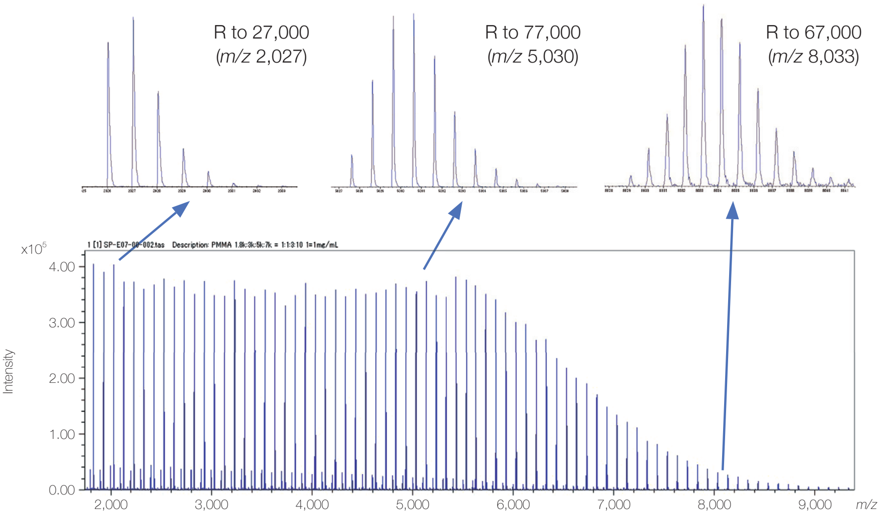
When a sample mixed with the matrix is irradiated with a pulsed UV laser beam, the matrix will absorb the laser energy and vaporize. At the same time, the sample will also be desorbed into the gas phase, which promotes the ionization process. Since primarily single-charge ions are generated, the horizontal axis of the mass spectrum corresponds to the mass of the ions, making interpretation of the spectrum straightforward. Due to its pulsed ionization nature and the need to analyze a wide mass range, it is well-suited for time-of-flight mass spectrometry (TOFMS) and is frequently used in polymer analysis.



Applications Measurement of Molecular Weight Distribution of Poly (methyl methacrylate)

The JMS-S3000 features spiral ion optics for precise polymer analysis over a wide mass range. It can also analyze terminal groups with high mass accuracy in each molecular region.



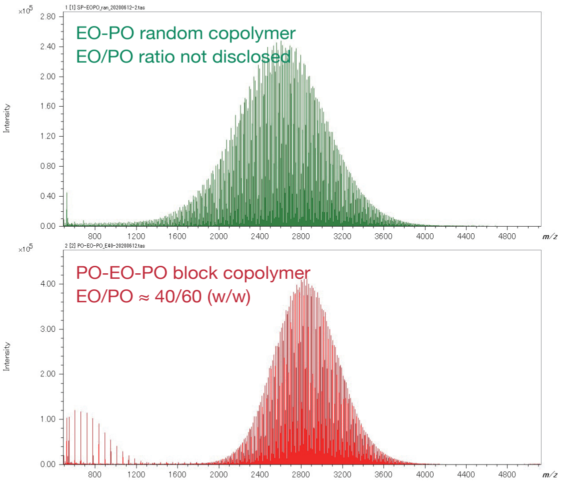


Sample: Poly (methyl methacrylate) (PMMA)

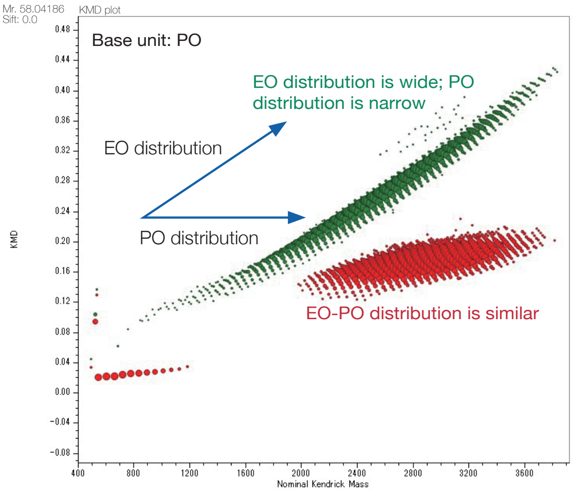
Applications Analysis of Binary Copolymers

Mass spectra of two types of EO-PO copolymers are shown below. The average molecular weights and the dispersities can be calculated from the mass spectra. The difference in the ratio of EO to PO can be known by analyzing the mass spectrum with the Kendrick mass defect (KMD), and the ratio of EO/PO can be calculated by creating degree of polymerization (DP) plots.

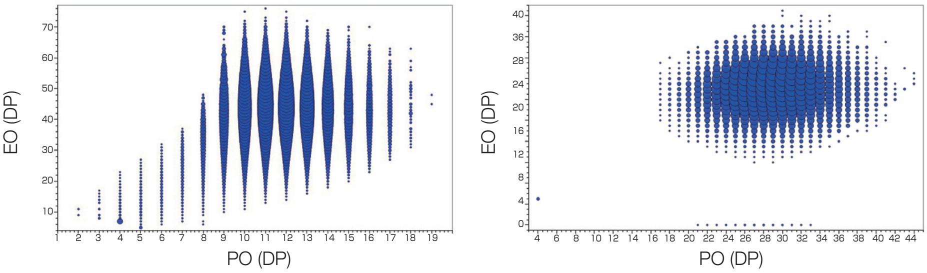
Mass spectrum



KMD plot



Degree of polymerization (DP) plot



Polymer index value

	PO-EO-PO	EO-ran-PO
Number-average molecular weight	2,562	2,863
Weight-average molecular weight	2,659	2,897
Dispersity	1.038	1.012
EO wt%	40.0	74.4

1-4 X-ray Fluorescence Spectrometer
XRF

The X-ray Fluorescence Spectrometer (XRF) enables analysis of constituent elements and compositions by detecting fluorescent X-rays emitted from a specimen irradiated with X-rays. For polymer materials, XRF is a quick and reliable method for quality control analysis in connection with product safety. It can be used for quick screening of residual catalyst used for polymerization, RoHS-restricted heavy metal elements (Cd, Pb, Hg, Cr and Br) as well as analysis of inorganic additive content used for functional improvement. Possible applications of the spectrometer also include analyzing inorganic surface treatment film deposits and thickness and identifying contamination mixed in during the manufacturing process. XRF is an element analysis instrument capable of easily analyzing elements that constitute a material in a non-destructive manner.

XRF

Non-destructive analysis

Analyzing any state of samples (solid, powder, liquid, etc.) without pre-treatment.

High-sensitivity detection

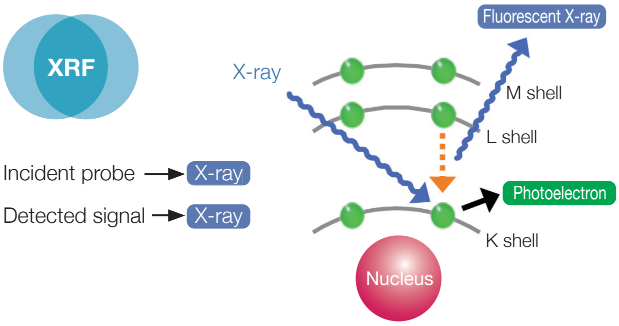
Detecting trace components on the order of ppm with eight types of primary filters and short-pass optical systems.

Standard-less quantification

The fundamental parameter (FP) method enables quantification of a wide range of components from trace to principal components with no standard sample. Enables measurement of the thickness of a thin film formed on the sample surface (plating, etc.).

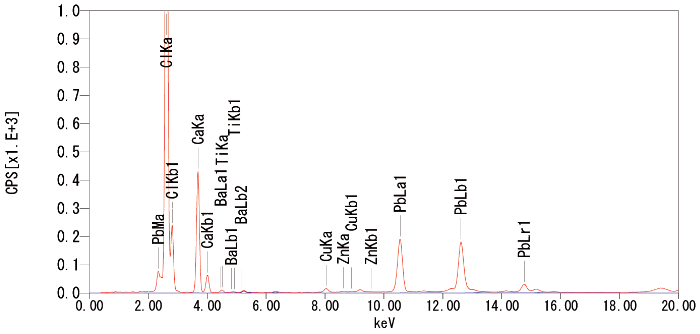
Principle Mechanism of fluorescent X-ray generation

When a specimen is irradiated with X-rays, electrons from the atoms within that specimen may be ejected. Outer shell electrons within those atoms will fill the vacancies caused by this irradiation and an X-ray of that discrete energy between outer shell and inner shell electron will be emitted. The energy of these Characteristic X-rays is measured to determine the elemental composition of a specimen.



Principal component Analysis of additives contained in soft PVC

Soft PVC is produced by adding certain additives (e.g. plasticizer, filler, stabilizer, and pigment) into a base PVC.
By considering plasticizer as the balance component, element components of other additives can be quantitatively determined.



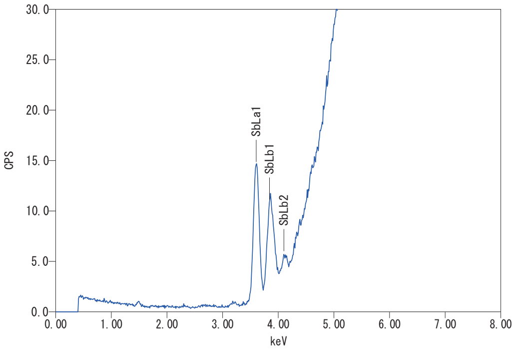
Component		Result
PVC	C_2H_3Cl	39.849
Filler	Ca	9.211
Stabilizer	Ba	0.054
	Pb	1.086
	Zn	0.012
Pigment	Cu	0.025
	Ti	0.018
Balance (plasticizer)	$C_{12}H_{19}Cl_2$	49.743

Unit: mass %

Trace component

Analysis of residual catalyst Sb in polyethylene terephthalate (PET)

Trace amounts of residual elements, used as catalysts for polymerization such as Sb and Ge, exist in the PET used for plastic bottles and food trays. XRF is capable of quickly analyzing such residual catalyst contents.



A high-precision analysis of any resin type can be made using the residual balance correction function in the FP method.

Component	Result
Sb	0.025
Balance (PET)	99.995

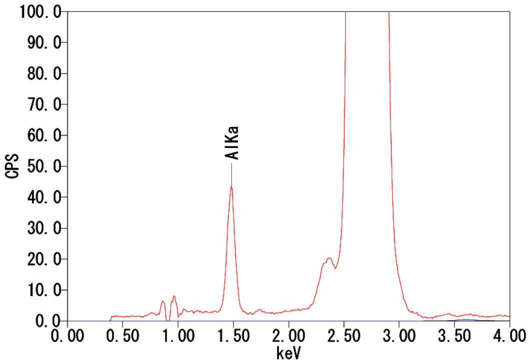
Unit: mass %

Surface treatment

Measurement of thickness of aluminum evaporated layer on PVC surface Measurement of Si deposits coated on PET surface

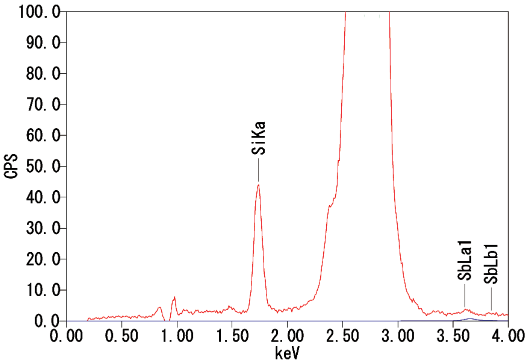
Some products have materials evaporated or coated on their surface for the purpose of improved functionality of water/heat resistance and mechanical properties, and for surface protection. The thin-film FP method enables the measurement of the thickness and deposit quantity of such surface treatment layers.

Thickness of Aluminum evaporated film



Component	Result
Aluminum layer thickness	44 nm

Quantity of Si deposits



Component	Result
SiO_2 quantity	0.0072 mg/cm^2

RoHS

Screening of heavy metal elements in products

RoHS Solution is dedicated software that incorporates optimal measurement conditions and FP quantification conditions. The software provides high-precision standard-less measurement results. The right figure shows measurement results of the IRMM ERM-EC681 pellet (2 mmϕ).

Sample EC681 Pellet

Note

Start at 29/12/2017 12:21:20

Element	Analysis value	3 σ	Unit	Judgement
Cd	121.6	21.4	ppm	GRAY
Pb	96.3	12.9	ppm	OK
Cr	104.7	7.7	ppm	OK
Br	782.5	29.2	ppm	GRAY
Hg	17.4	8.8	ppm	OK

Total remaining time 00:00:00

Remaining time 00:00:00

1-5 X-ray Photoelectron Spectrometer

XPS

The X-ray Photoelectron Spectrometer (XPS) is an analysis instrument capable of quantitative, qualitative, and chemical-bonding state analyses of the top surface of a substance by analyzing photoelectrons that are generated when a specimen is irradiated with X-rays. Other applications of XPS include specimen surface cleaning by ion irradiation and internal structure analysis by repeated measurement and etching.

XPS

Surface analysis instrument

Analyzes the top surface of a substance. The depth of analysis is approximately 6 nm.

Quantitative analysis and chemical-bonding state analysis

Performs quantitative analysis from the obtained spectrum peak intensity and identification of the chemical-bonding states from peak positions and peak shapes.

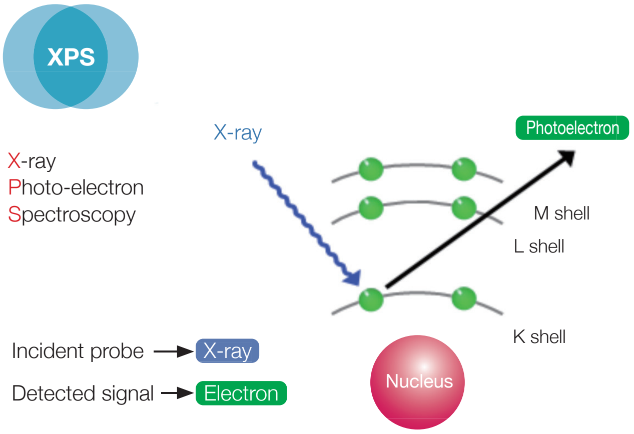
Depth profile analysis

Performs depth profile analysis of element distribution and interface characterization when combined with ion etching.

Principle Mechanism of photoelectron generation

Basic information obtained with XPS

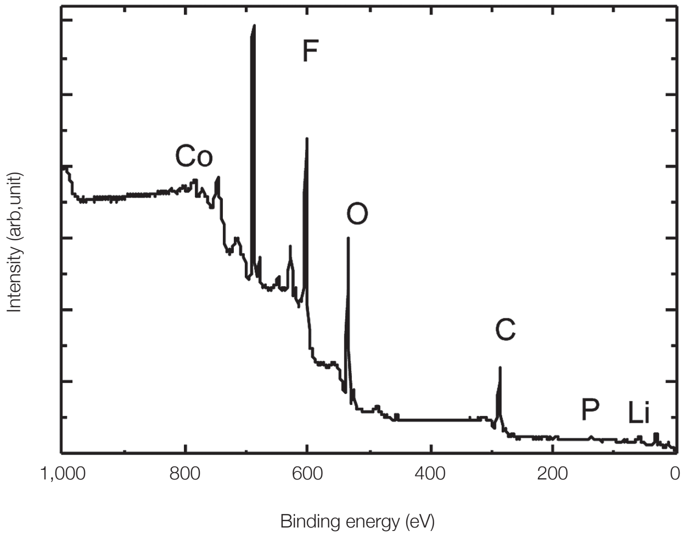
- Signal positions (horizontal axis):
  Element information (qualitative analysis)
- Signal intensity (vertical axis):
  Integrated values (quantitative analysis)
- Precise signal positions and shapes (split)
  Chemical shift (chemical-bonding state analysis)



Applications

Analysis of Li-ion battery surface

A positive electrode of a lithium-ion battery was analyzed. From the electrode surface, electrolyte components such as Li, C, O, F, and P, and an active material, Co, were detected.



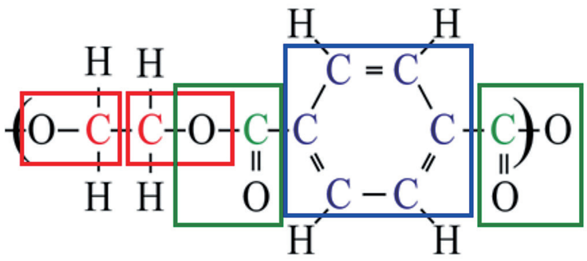
Sample: Li-ion battery positive electrode surface

Applications

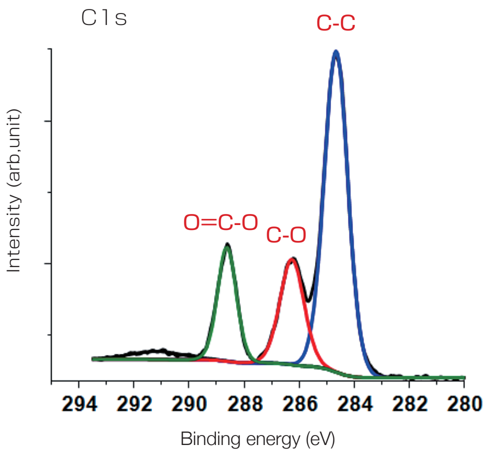
Analysis of polyethylene terephthalate (PET)

Analysis of polymer materials by XPS also provides information on functional groups of the materials; peaks of each functional group can be found by observing the relevant spectrum obtained by XPS. In this case, the benzene ring, carbonyl group and carboxyl group which are contained in PET were detected.

Chemical structure formula of PET



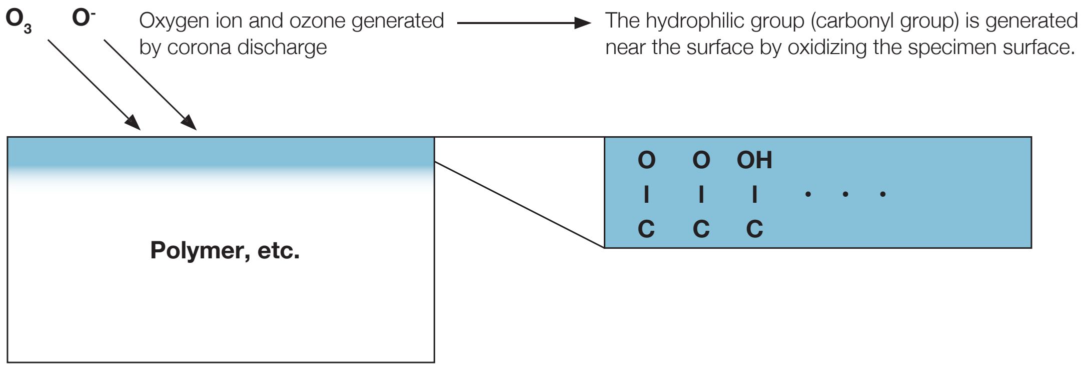
C1s spectrum of PET obtained by XPS



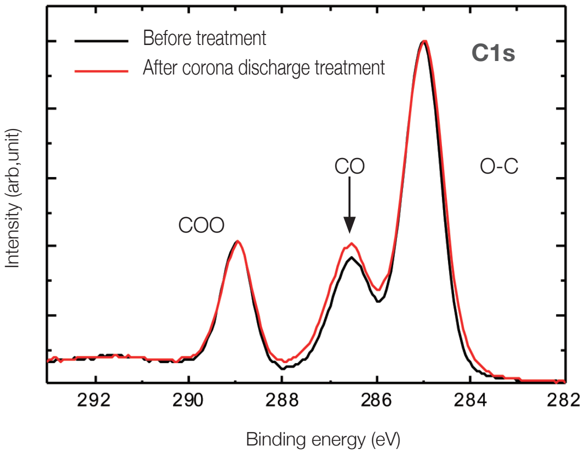
Applications Evaluation of surface-treated polymer material

Polymer materials are often used in combination with other substances as composite materials. Bonding strength plays an important role for such applications and it can be increased by various surface treatments that are applied to the bonding surface, e.g. discharge and addition of substances of various properties. Qualitative and quantitative analyses by XPS are useful for the evaluation of surface treatment agents applied to polymer materials.

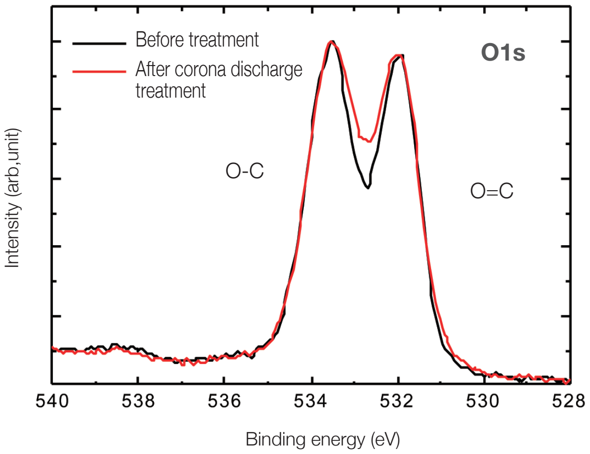
Schematic of surface treatment of polymer material



Changes in surface conditions due to corona discharge treatment



C1s spectrum



O1s spectrum

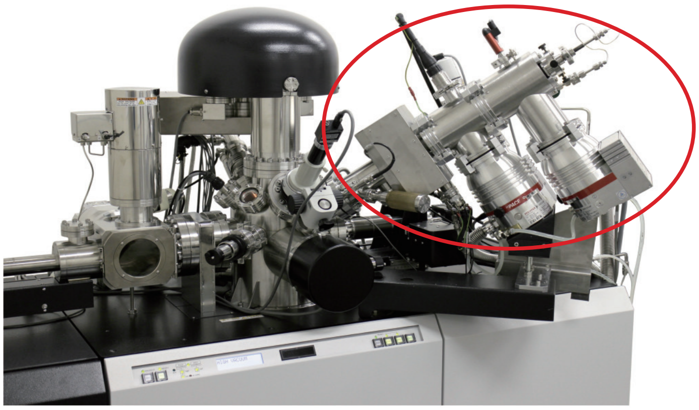
PET film measurement data obtained by XPS before and after corona discharge show that the peak intensity of CO was increased after the treatment. It is thought that higher hydrophilicity was caused by the increased CO level because corona discharge treatment on PET is known to increase hydrophilicity.

Option

XPS depth profile analysis by ion irradiation - XPS application using cluster ion beam -

XPS is capable of performing a depth profile analysis on polymer materials by alternating between ion-irradiated sample etching and XPS analysis. In recent years, cluster ion-beam irradiation units designed to hit an ion cluster onto a sample have expanded its applications. As etching causes only minor chemical damage to an organic sample when it is irradiated with a cluster ion beam, cluster ion-beam irradiation can be an effective technique for performing a depth profile analysis of polymer materials and cleaning of surface contamination.

JPS-9030+GCIB10s



Cluster ion irradiation unit
GCIB10s

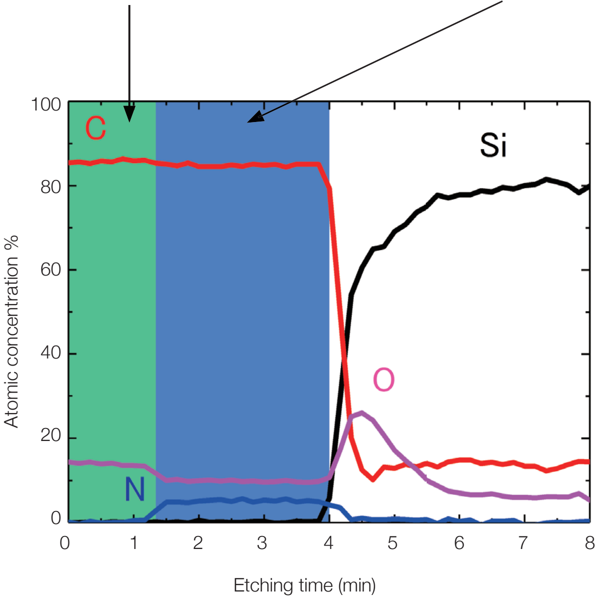
Applications

Depth profile analysis of a polymeric multi-layer film

A depth profile analysis was conducted using a combination of cluster ion beam and XPS. As a result, the layer structure of a polymeric multi-layer film was successfully analyzed at superior depth resolution of sub-10 nm.

BASF IRGANOX 1010 layer: 50 nm

BASF IRGANOX 3114 layer: 150 nm



【Reference】JEOL Application Note: HS-004

1-6 Scanning Electron Microscope

SEM

The Scanning Electron Microscope (SEM) is an instrument for imaging the specimen surface by irradiating it with a focused electron beam and performing a two-dimensional scan. The SEM detects various signals including secondary electrons, backscattered electrons and characteristic X-rays generated by electron beam irradiation to obtain morphology of the specimen surface, crystalline information and chemical information (composition, etc.). Owing to ease of operation for morphological observation and local area analysis of bulk specimens, the SEM is widely utilized in various applications ranging from basic research to industrial use.

Morphological observation

Obtains morphological information on the specimen surface through a secondary electron image.

Compositional observation

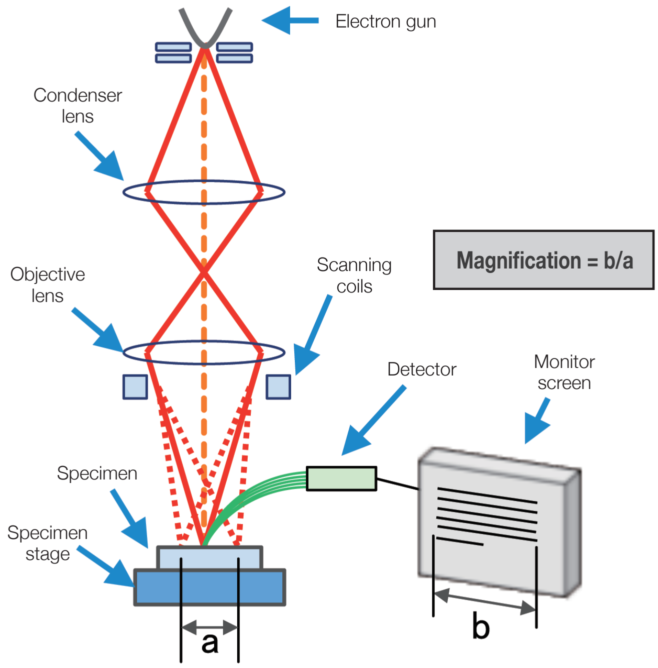
Obtains compositional information on materials through a backscattered electron image.

Elemental analysis

Obtains information on constituent elements of the specimen by detecting characteristic X-rays.

Principle

The SEM uses a condenser lens and an objective lens to focus the electron beam produced by an electron gun onto a specimen surface. The scanning coils then scan the electron beam in the X and Y directions and the detector acquires signals generated from the specimen. The monitor screen is synchronized with the electron beam scanning for observation.
The magnification of SEM image is determined by the electron beam scanning width "a" and the image display width "b".

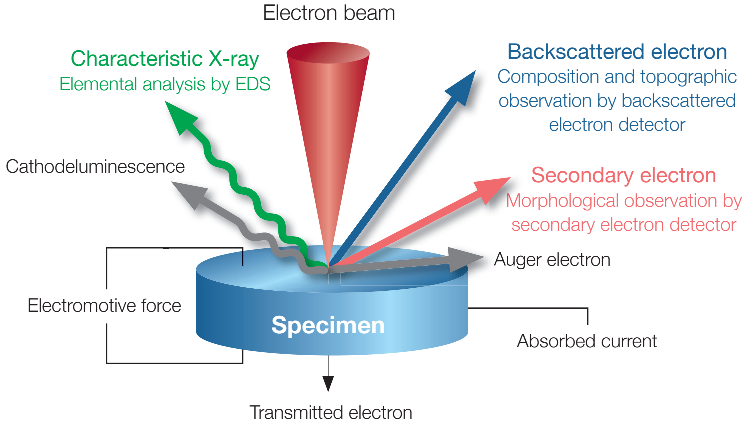


Schematic of SEM configuration

Signals

Various signals are emitted from a specimen when it is irradiated by the electron beam, and such signals are converted into the required information by detectors.
Different detectors are used to obtain the target information.

Various signals generated from a specimen by electron beam irradiation



Applications

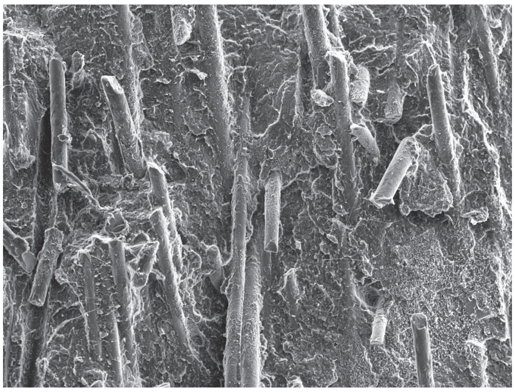
Observation and analysis of reinforced plastic

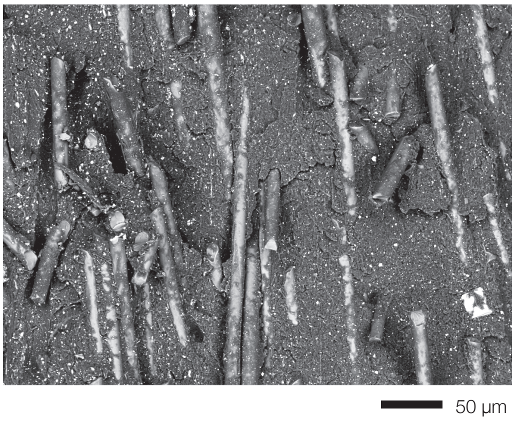
Morphological observation

Morphology of a fractured specimen was observed by a secondary electron image.

Composition observation

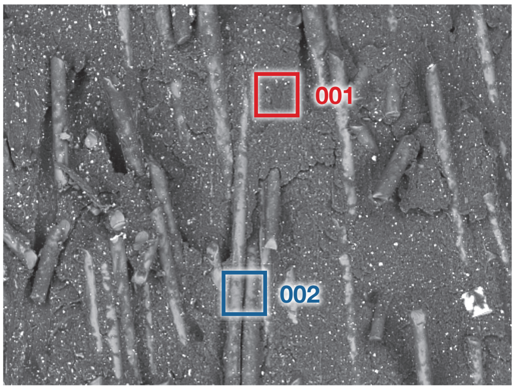
The same region acquired as a secondary electron image was observed by a backscattered electron image. As a result, the different compositional contrast between fillers and substrate were obtained. It clearly reveals filler distribution and orientation.

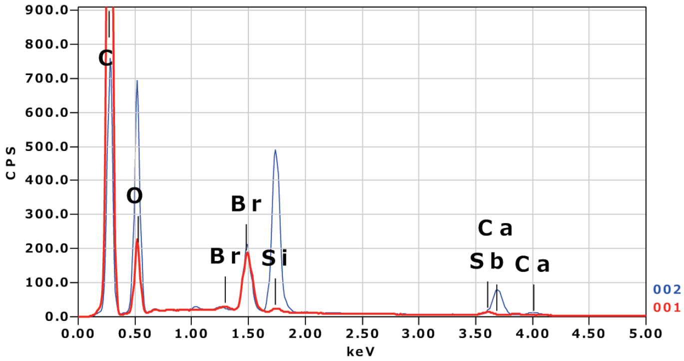




Elemental analysis

The following elemental analysis result by EDS shows the existence of Si and Ca in the filler.
You can compare elemental information on any region by point EDS analysis.





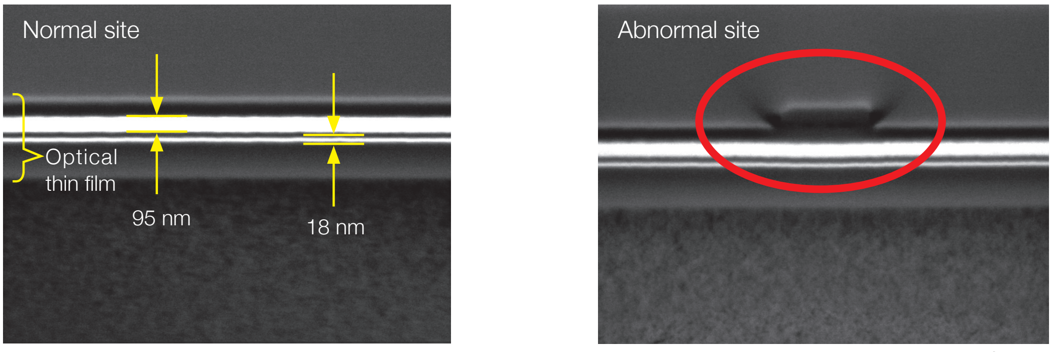
Specimen: Reinforced plastic

Applications Observation and analysis of polymer materials

Observation

Observation of defects on a plastic lens

The cross section of a plastic lens was treated by Focused Ion Beam (FIB). These SEM images enable the thickness of each optical thin film to be measured. SEM observation revealed that a defect (encircled in red) was deposited to the optical thin film at a site recognized as being abnormal.

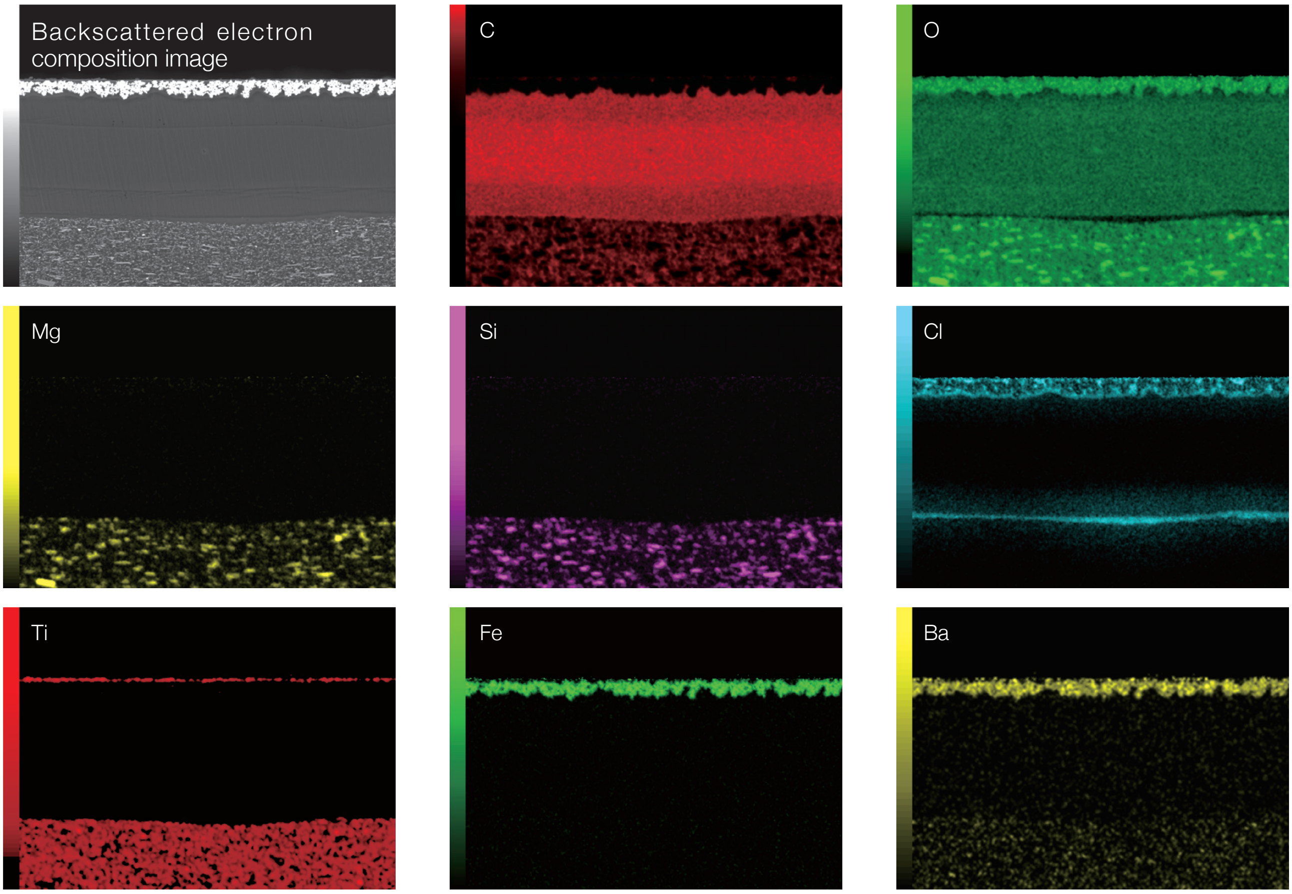


Specimen: Plastic lens (blue-light cut glass)

Elemental analysis

Cross sectional analysis for plastic card

EDS elemental maps of the cross section of a plastic card, to which a magnetic tape layer was adhered, were acquired. From the maps, it was found that a few layers with slightly different quantities of C and O exist beneath the magnetic tape layer in which large quantities of Fe and Ba are dispersed.

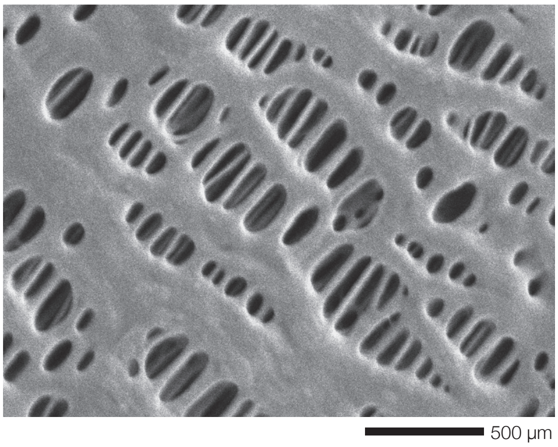


Specimen: Plastic card (with a magnetic tape layer)

Observation at ultra-low landing voltage

Separator observation

Observation at extremely low voltage eliminates charging and electron beam damage. The image below shows clearly surface morphology on a separator at extremely low voltage of 0.05 kV.

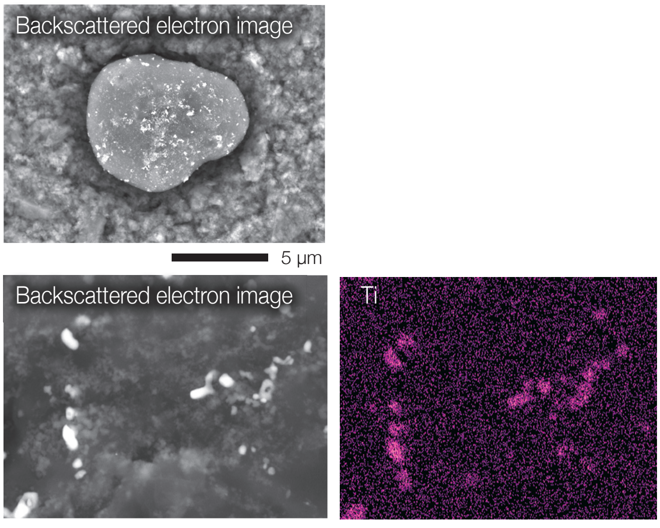


Specimen: Polypropylene separator in Li-ion battery
Extremely low landing voltage of 0.05 kV.

Low-vacuum SEM

Toner particle analysis

Observation in low vacuum is useful for Insulators because it is easy to reduce charging by this method. It is possible to observe and analyze non-conductive specimens without a conductive coating.



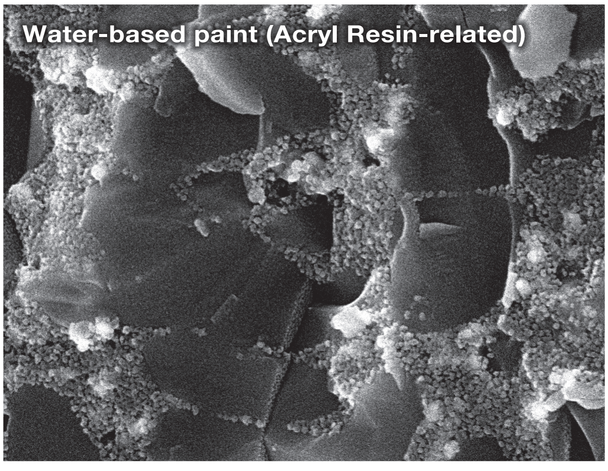
Specimen: Toner
landing voltage: 7 kV Vacuum: 70 Pa

Cryo-SEM

Observation of hydrated specimens - Cryo-SEM

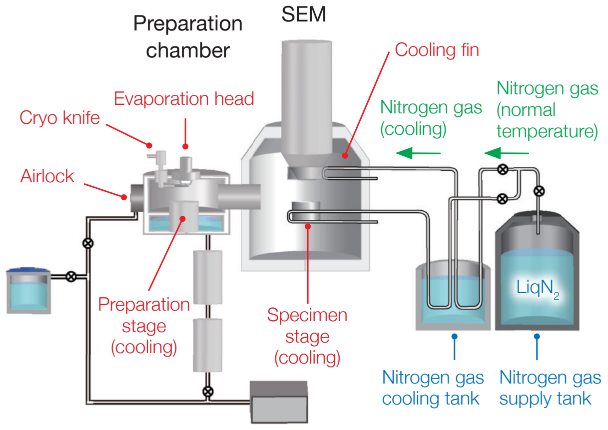
The Cryo-SEM method enables the observation of hydrated specimens while preserving their morphologies by freezing them. In this method, a rapidly-frozen specimen is freeze-fractured or etched in a preparation chamber to expose the intended inner face of the specimen. The specimen is then introduced to the SEM stage for observation while it is cooled at liquid-nitrogen temperature.

Morphological observation



Rapid freezing (Liquid Nitrogen) Freeze fracturing
Etching Evaporated Au Cryo-SEM Observation

Schematic of Cryo-SEM



Liquid-state acrylic polymer emulsion was observed with the Cryo-SEM. While hydrated specimens are unavoidably deformed in normal-temperature SEM observation, the Cryo-SEM method allows such specimens to be observed in their native morphological structures by freezing them.

1-7 Transmission Electron Microscope TEM

The transmission electron microscope (TEM) is an instrument for observing the internal structure of a specimen by passing an electron beam through a thin film specimen. The thickness of the specimen for TEM is less than 100 nm. Generally, since the polymer material is composed of light elements, it is necessary to perform staining with heavy metals. In addition to observing fine structures, TEM can also perform electron diffraction to determine the crystal state of the specimen, elemental analysis, and three-dimensional reconstruction by the tomographic method.

TEM

Fine structure observation

TEM can perform tissue observation at low magnification to observation at atomic resolution.

STEM observation

A scanning transmission electron microscope (STEM) image can be acquired by scanning a small electron probe on a specimen.

Elemental analysis and electron diffraction

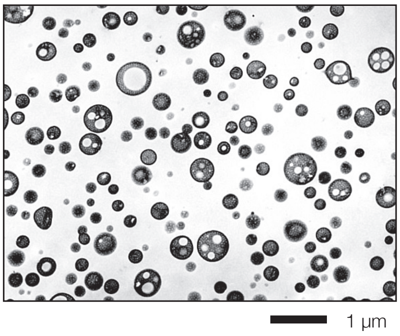
Analysis and electron diffraction are possible in regions of several nm or less.

Cryo-observation

Low temperature observation of a weak specimen susceptible to breakage by electron beam irradiation.

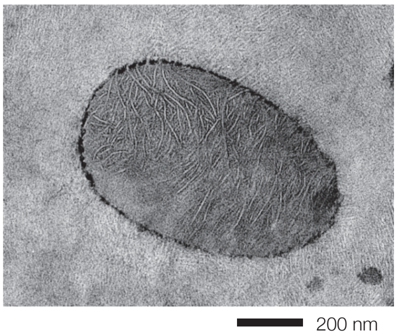
Observation example

Phase-separated structure



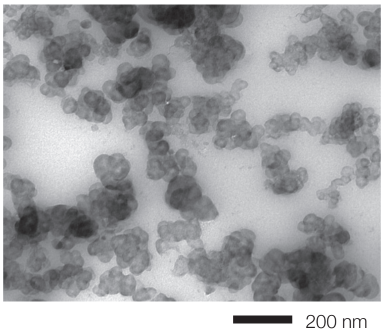
Specimen: ABS resin
Specimen preparation: Ultrathin sectioning
OsO_4 staining

Lamellar structure of crystalline polymer



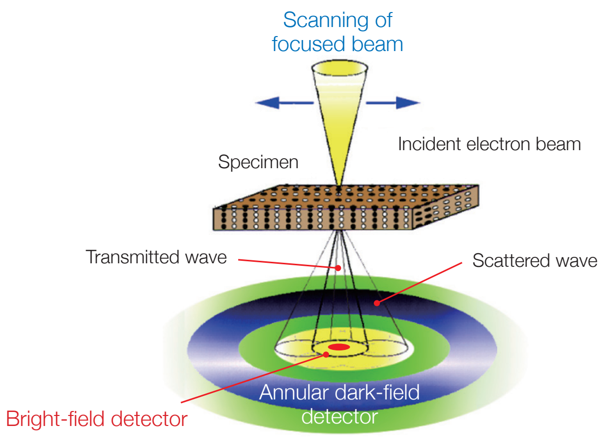
Specimen: Blended polymer (PE/PP)
Specimen preparation: Ultrathin sectioning
RuO_4 staining

Filler dispersion in rubber



Specimen: Filler composed of styrene-butadiene rubber (SBR) + carbon black
Specimen preparation: Cryo ultrathin sectioning
No staining

Principles of STEM

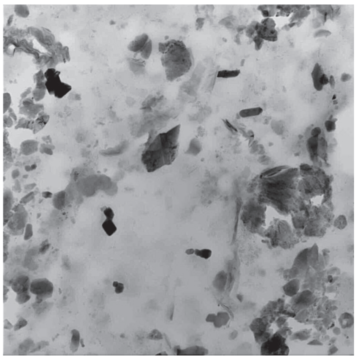


Transmitted electron: bright-field (BF) image
Scattered electron: dark-field (DF) image

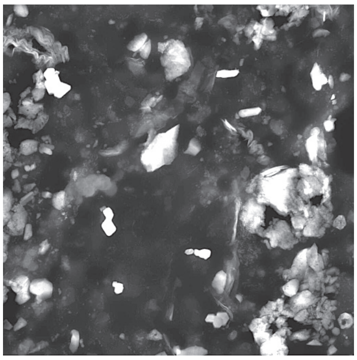
Observation example

STEM observation and EDS analysis of filler in rubber

STEM BF image

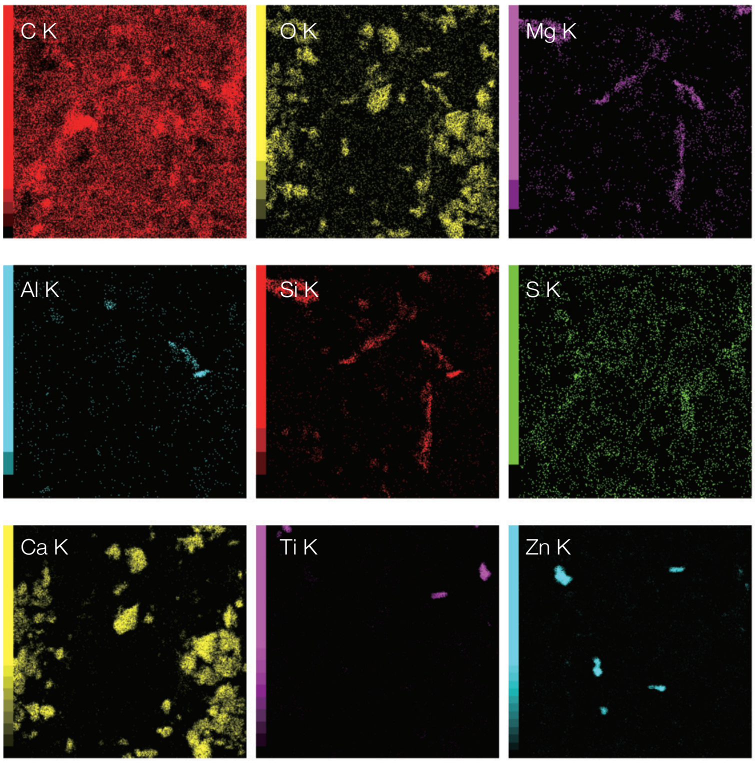


STEM DF image



1 µm

Elemental analysis by EDS



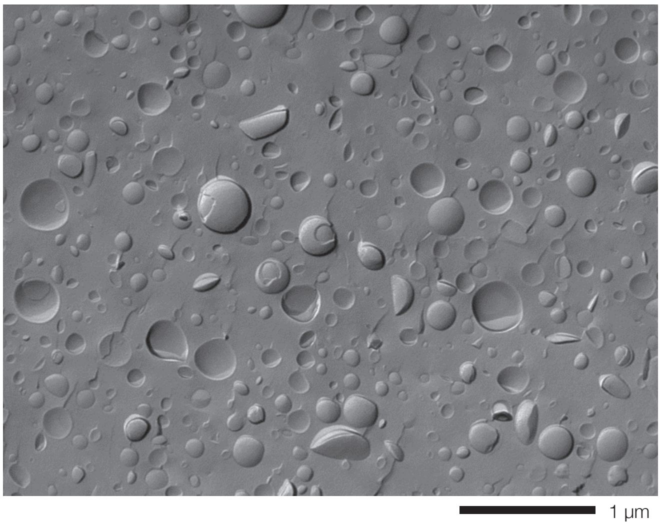
2 µm

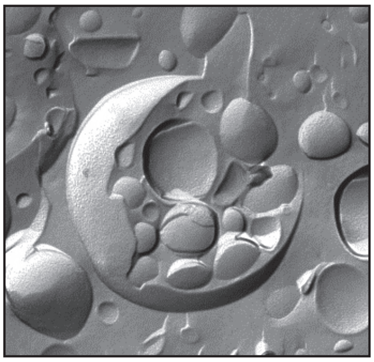
Specimen: Rubber plug

Observation example

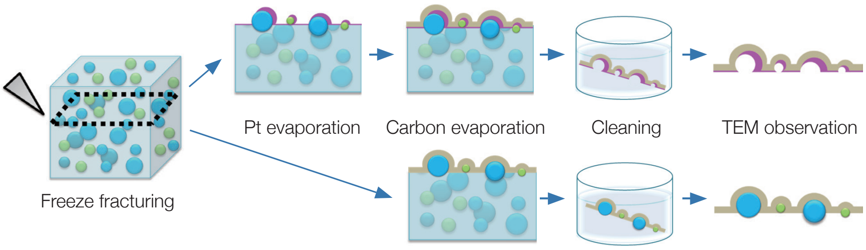
Observation of a specimen in liquid solution: emulsion

Freeze fracturing - Replica method





Specimen: Emulsion



Freeze-fracturing - Replica method

A rapidly-frozen specimen is fractured in a high vacuum and a replica film of the fractured surface is observed by the TEM.

Freeze-fracturing - Extraction replica method

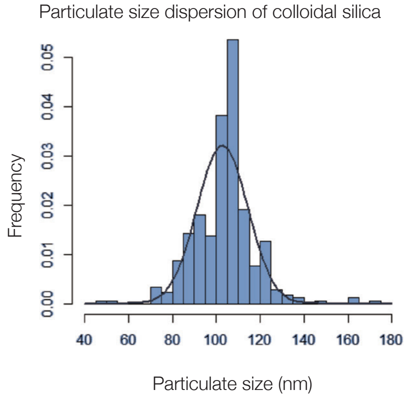
A rapidly-frozen specimen is fractured in a high vacuum and carbon is evaporated on the fractured surface. Then particles embedded in the evaporated film are observed by the TEM.

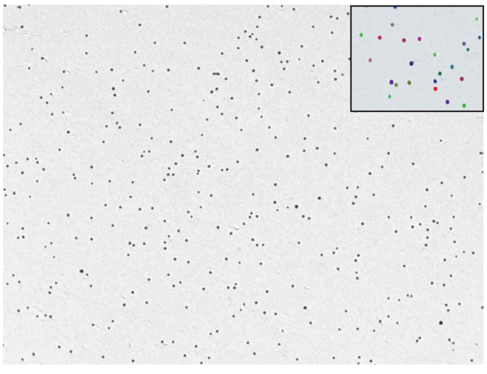
Observation example

Measurement of particulates dispersed in liquid solution

Freeze-fracturing - Extraction replica method

Particulates dispersed in a liquid solution condense when dried and it is difficult to grasp the original state of dispersion. However, rapid freezing physically fixes specimens dispersed in the liquid solution, allowing for the observation of dispersion and aggregation states in water.





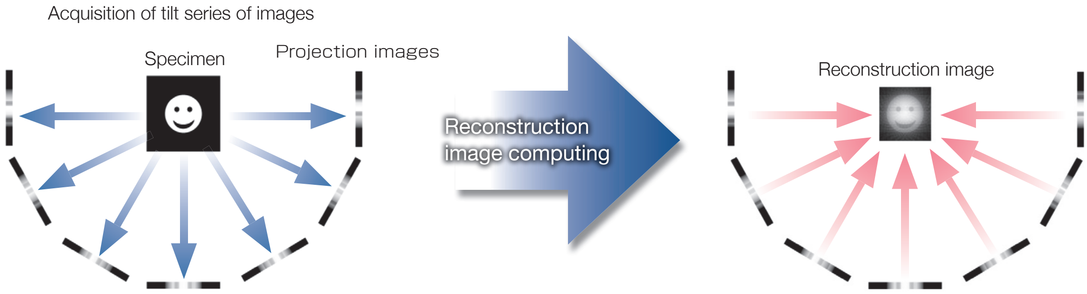
Specimen: Colloidal silica

The result shows how colloidal silica particulates are dispersed without being condensed.

Three-dimensional structure reconstruction

TEM tomography is a technique for reconstructing a three-dimensional structure from an acquired sequential tilt-series of projection images, similar to X-ray CT technology used in the medical field. Specimens subject to TEM observation are as thin as sub-100 nm. But compared with the spatial resolution (1 nm or less) of the TEM, this thickness is large. Computer processing of such tilt series of images acquired by TEM tomography allows for reconstruction of the three-dimensional structure inside a specimen at a nanoscale resolution.

Acquisition of tilt series (projection) of images

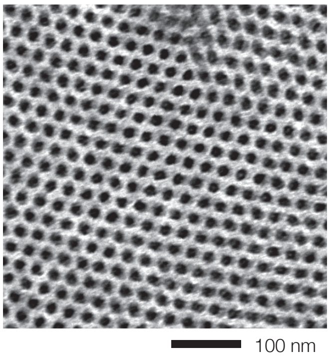


Observation example

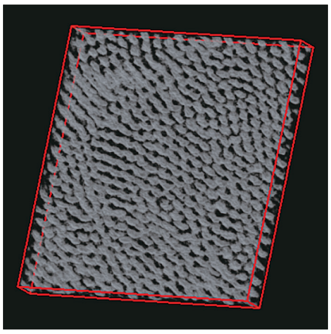
Three-dimensional reconstruction by TEM (TEM tomography)
Three-dimensional structure of block copolymer

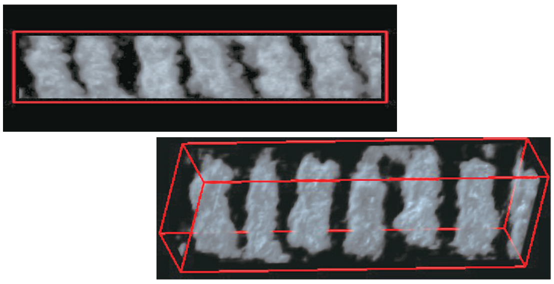
Three-dimensional structures of two different types of block copolymer were reconstructed using TEM tomography. While the specimens are not distinguishable in two-dimensional images, the three-dimensional reconstruction images clearly show their differences.

Cylindrical structure (TEM image)

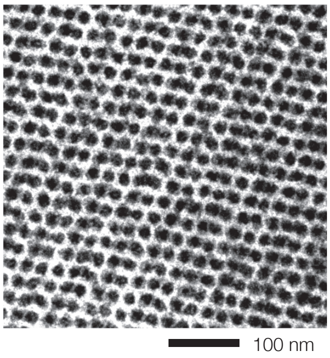


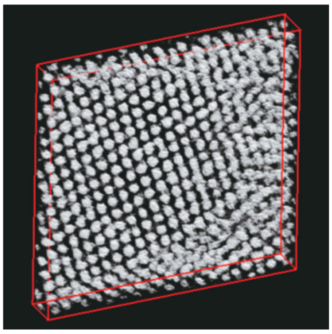
Three-dimensional reconstruction image (black-and-white-inverted)

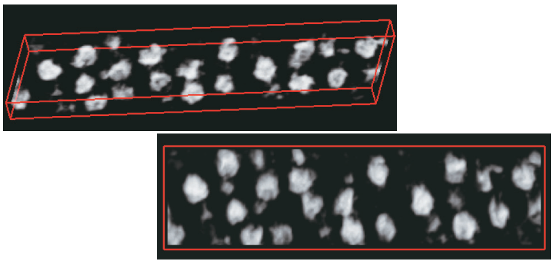

(x, y, z) = (507, 507, 47 nm)


Single row

Spherical structure (TEM image)




(x, y, z) = (661, 661, 88 nm)



Specimen: Poly (styrene-block-isoprene)
Specimen preparation: OsO_4 staining, ultrathin sectioning
Tilt angle: -60° to +60° (1° steps)
Data courtesy: Professor Hiroshi Jinnai, Tohoku University

Cryo-TEM

Samples prepared by various freezing techniques, such as ice embedding and frozen sectioning, are inserted into an electron microscope and observed in a frozen state. Observation is performed at liquid nitrogen or liquid helium temperature.
There are two methods: one using a cryo-transfer holder and the other using a cryo-TEM equipped with an automated specimen transfer system.

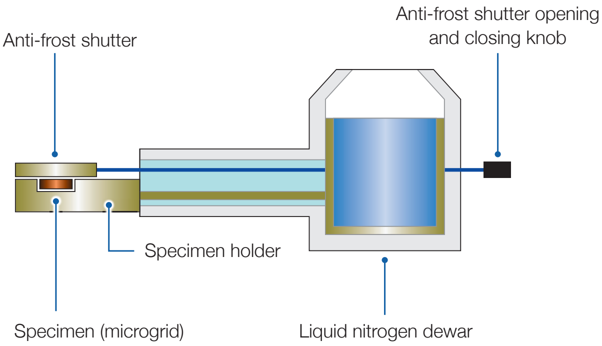
Cryo-TEM

The specimen stage in the electron microscope, the transfer system, and the storage unit are always cooled with liquid nitrogen for cryogenic observation.
Samples can be transferred automatically at liquid nitrogen temperature by using the transfer system.
In addition, the storage unit can store 12 frozen samples at liquid nitrogen temperature.

Cryo-TEM

Cryo-Transfer Holder

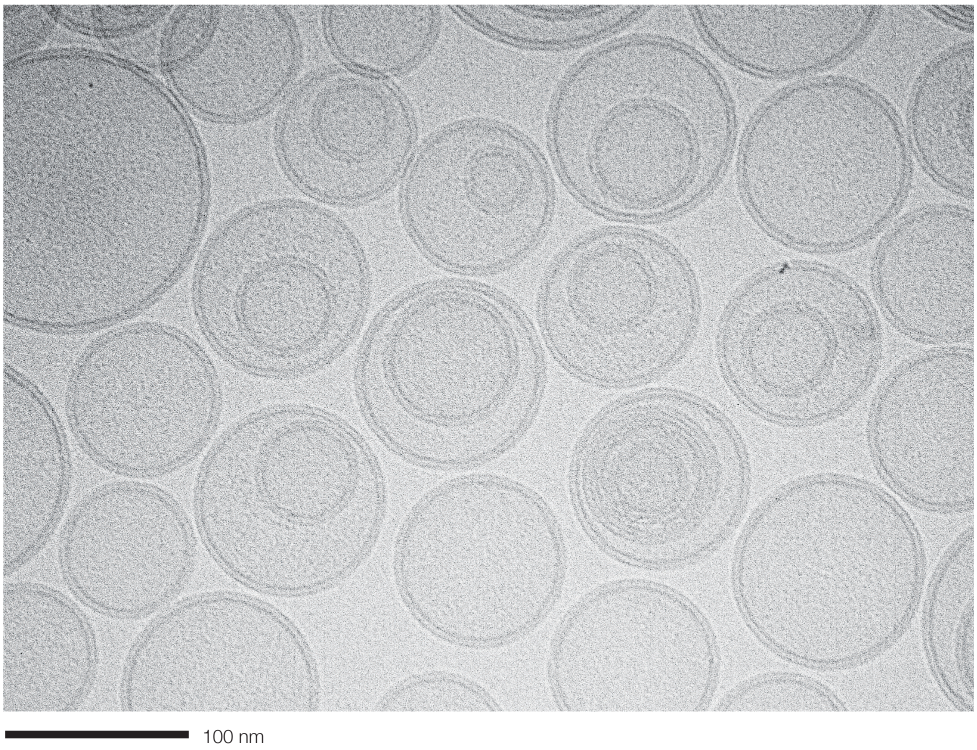
This holder enables the observation of samples frozen by the ice embedding method at ultra-low temperatures.
It can be used in TEM, SEM, and FIB.
It is equipped with a liquid nitrogen dewar and the tip is kept at liquid nitrogen temperature. It is equipped with a shutter that isolates the tip from the outside air to prevent frost from adhering to the sample when inserting the holder into the electron microscope.



Observation example

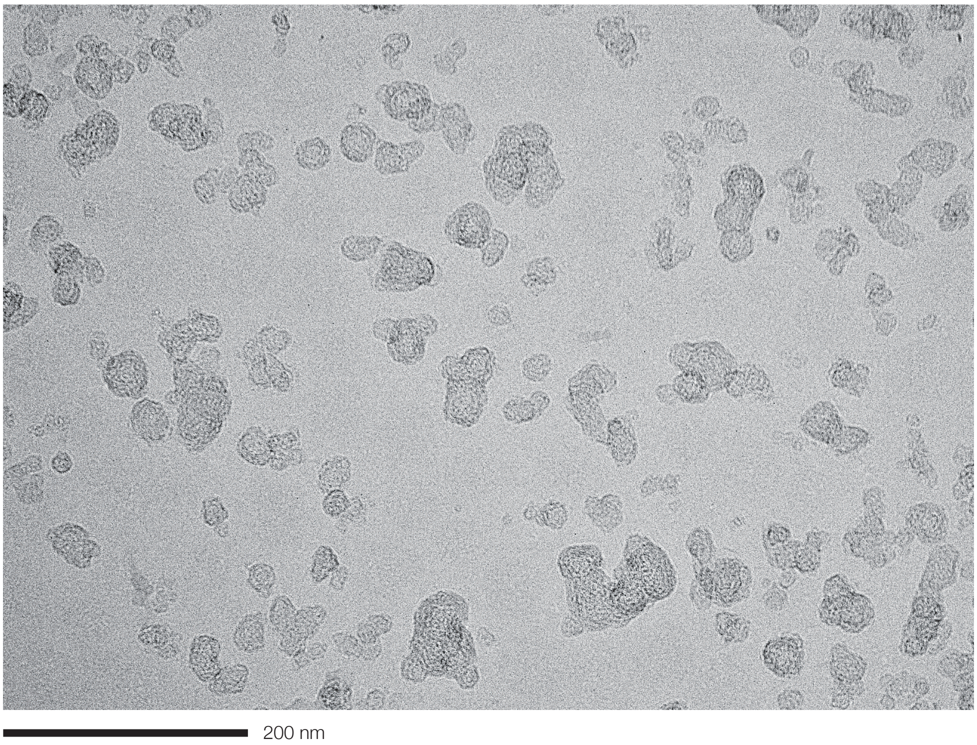
The following are examples of TEM observations of solution samples in a frozen state after rapid freezing.

Structure of liposomes in solution



Specimen: Liposomes
Specimen preparation: Ice embedding

Dispersity of carbon black



Sample: Ink-based material
Specimen preparation: Ice embedding

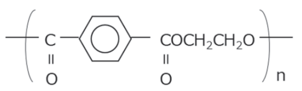
YOKOGUSHI Applications
Analysis of Polyethylene Terephthalate

Polyethylene terephthalate (PET) is a thermoplastic polyester widely used in food packaging, beverage containers, textiles, and many other applications. For example, PET provides excellent transparency, lightness, and durability as a material for beverage bottles and food containers, ensuring product protection and safety. In addition, PET fibers are used in clothing and household goods and are useful in situations where durability and flexibility are required.

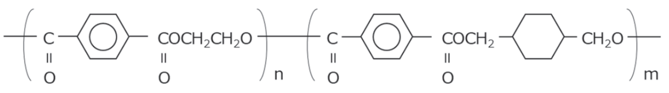
Degradation analysis is essential for quality control and long-term performance of PET products. PET may deteriorate due to environmental and chemical factors, and its physical and chemical properties may change. Degradation analysis can evaluate the durability and safety of products and improve manufacturing processes and materials. It is also important from the perspective of environmental impact and reusability, and it is part of the effort to develop sustainable products.

2-1 Characterization of Crystalline and Amorphous PET

Type	Features
C-PET	Crystalline PET. It has a high density due to the regular arrangement of the molecules in the crystallized part and is characterized by high strength and heat resistance.
A-PET	Amorphous PET. It is characterized by high impact strength and easy bending. However, changes in density over time can cause internal stress, which can break the polymer chains, resulting in a decrease in flexibility, impact resistance, and strength.
Glycol-modified PET (G-PET, PETG)	Approximately 30 to 40% of the ethylene glycol in the PET resin is replaced by cyclohexane dimethanol. It is classified as amorphous PET because the polymer does not crystallize during molding.



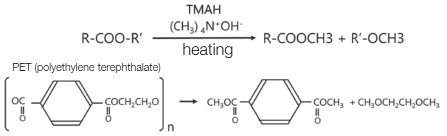
C-PET
A-PET

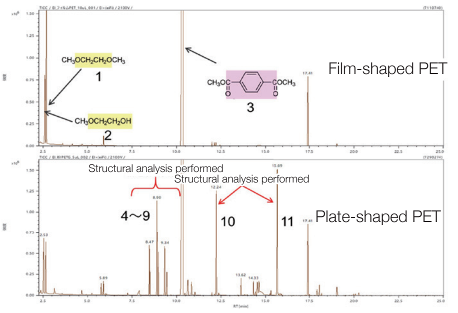


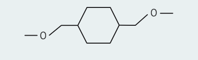
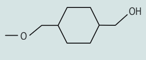
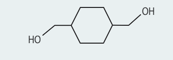
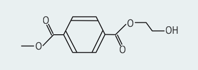
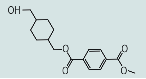
G-PET

Analysis by Reactive Pyrolysis GC-MS

For condensation polymers, the reactive pyrolysis GC-MS method is effective, in which reaction reagents such as acids and alkalis coexisting with the sample are introduced into the instrument to selectively break the ester bond, followed by hydrolysis and functional group derivatization at the same time.
The figure shows the total ion current chromatograms (TICC) by the EI method for plate-shaped PET and film-shaped PET during reactive pyrolysis. Several peaks were observed in the plate-shaped PET that were not in the film-shaped PET. Peaks 4 to 9 are reaction pyrolysis products derived from cyclohexane dimethanol, and 3 different methylation numbers and 2 structural isomers were observed from the integrated analysis results of EI and FI.

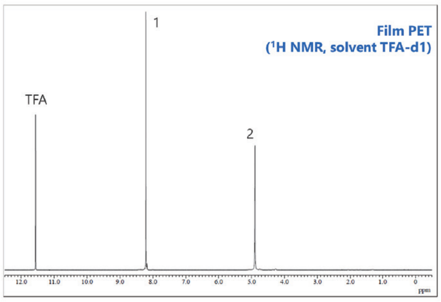


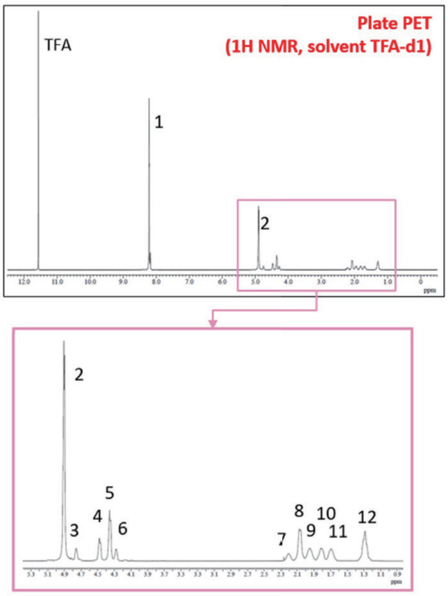


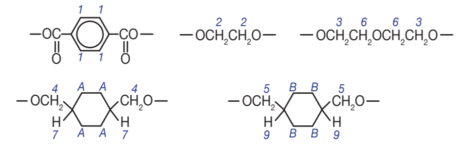
Peak#	4,5	6,7	8,9
Structure			
Peak#	10	11	
Structure			

Analysis by Solution NMR

According to the results of reactive pyrolysis GC-TOFMS, assuming that the plate-shaped PET was G-PET, a comparison with the NMR library of PolyInfo [1] was performed. As a result, it showed very good agreement with the PETG spectrum in the library, and it was possible to analyze the structure of the plate-shaped PET. In particular, structural isomers were able to be distinguished by NMR. In addition, the ratio of ethylene glycol to cyclohexanedimethanol was about 2:1 from the peak ratio.



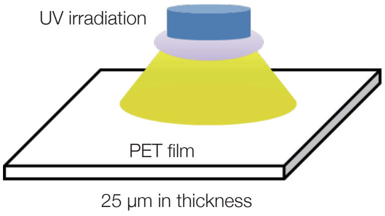




A:11(axial) or 10 (equatorial) A:12(axial) or 8 (equatorial)

2-2

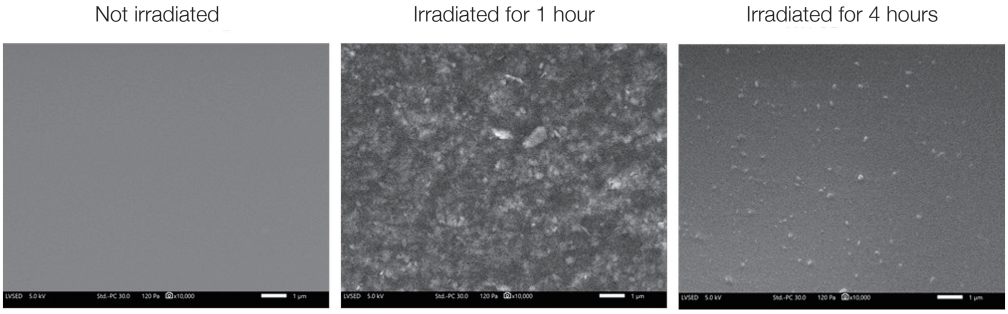
UV Degradation Analysis of PET Film



The sample was a commercially available polyethylene terephthalate (PET) film.
UV was irradiated onto one side of the PET film by using a UV curing device HANDY CURERUB (manufactured by SEN LIGHTS Co., Ltd., illuminance of 170 mW/cm^2).

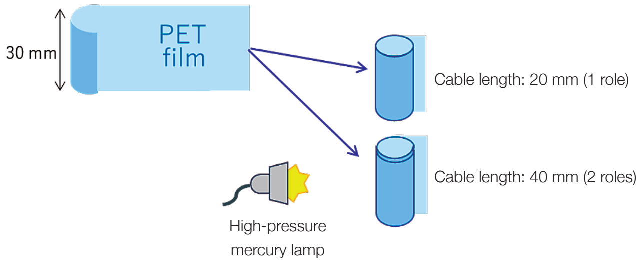
Surface Observation by SEM

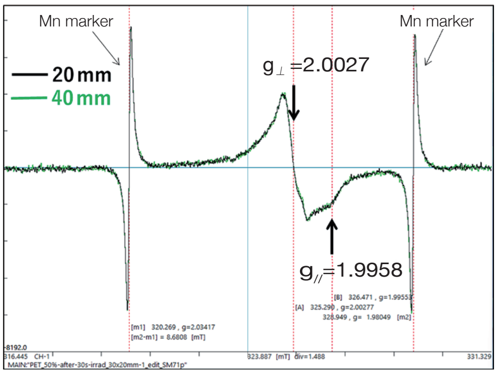
Low-vacuum secondary electron images were used to confirm the changes over time on the sample surface. It was confirmed that the surface morphology of the PET changed as it was irradiated with UV for 1 to 4 hours. In this way, by using the low-vacuum function, even polymer surfaces can be observed without a conductive coating.



Observation by ESR of Radicals Formed in PET Film Irradiated with Light

The obtained signal, after being corrected and normalized with the Mn markers measured simultaneously, showed $g_{\perp} = 2.0027$ and $g_{//} = 1.9958$. This indicated the formation of carbon radicals. In the figure on the right, the spectrum obtained from a sample of twice the length is superimposed. Since the intensity was identical, it was shown that the light that decomposes the PET was shielded only on the very surface.



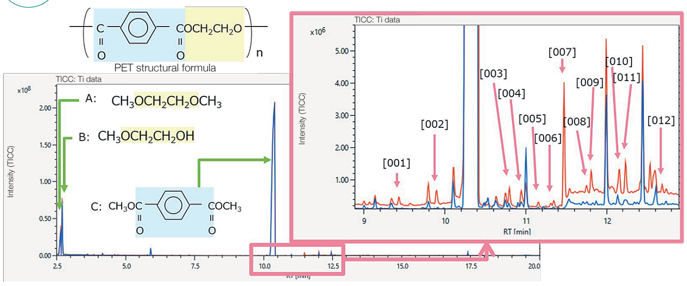


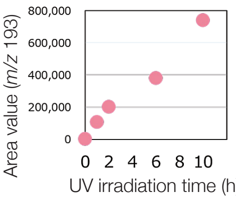
Structural Analysis of the Main Chain by Reactive Pyrolysis GC-MS

Three components (A, B, C) were strongly detected as reactive pyrolysis products derived from the main chain of PET. These were common components before and after UV irradiation.

As a result of performing a two-sample differential analysis of the samples before and after UV irradiation, 12 components shown in the TICC at RT of 9 to 13 minutes were extracted as differential components. An extracted ion chromatogram (EIC)* was created at the base peak of ID: 007, which was a characteristic component after UV irradiation and was the strongest, and the change of area value with respect to UV irradiation time was confirmed. As a result, it was found that the area value increased according to the UV irradiation time, and the change due to UV irradiation in a short period of time was also detected. In addition, as a result of structural analysis by GC-TOFMS, ID: 007 was estimated to be a pyrolysis product derived from the photooxidation reaction by UV irradiation.

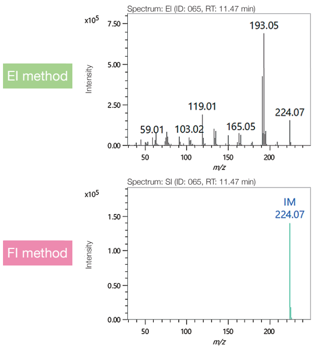
TICC by EI method (blue: 0 h, red: 10 h)





*Note: EIC creation conditions: *m/z* 193.050, *m/z* depth: ±0.05 Da

Mass spectrum



Accurate mass analysis results

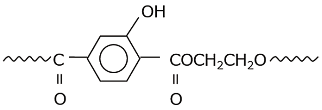
Fragment ion generated by EI

m/z	chemical formula	DBE	mass error [mDa]
45.03345	C2 H5 O	0.5	-0.04
59.01263	C2 H3 O2	1.5	-0.13
63.02280	C5 H3	4.5	-0.12
75.02285	C6 H3	5.5	-0.07
76.03060	C6 H4	5.0	-0.15
91.01754	C6 H3 O	5.5	-0.30
103.01755	C7 H3 O	6.5	-0.29
119.01246	C7 H3 O2	6.5	-0.30
133.02804	C8 H5 O2	6.5	-0.37
150.03058	C8 H6 O3	6.0	-0.56
165.05394	C9 H9 O3	5.5	-0.68
191.03344	C10 H7 O4	7.5	-0.45
193.04923	C10 H9 O4	6.5	-0.31

Molecular ion generated by FI

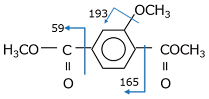
m/z	chemical formula	DBE	mass error [mDa]
224.06781	C11 H12 O5	6.0	-0.11

Structural formula in reference



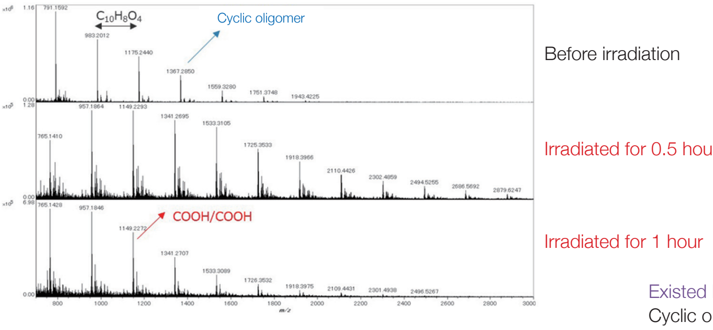
G. J. M Fechine *et al.*, J. Appl. Polym. Sci., **104**, 51-57 (2007).

Estimated structural formula for ID: 007

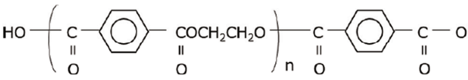


Analysis of Terminal Groups of Oligomers on Sample Surface by MALDI-TOFMS

Before UV irradiation, cyclic oligomers were mainly observed. After UV irradiation of 0.5 hour, there were almost no cyclic oligomers, and the main components were a series presumed to have a carboxyl terminus derived from a photooxidation reaction. This series showed a decrease in molecular weight after 1 hour of UV irradiation. The distribution of Series I and II on the PET film also revealed the areas of degradation due to UV irradiation. By standardizing the mass image of Series II with the mass image of Series I that existed before UV irradiation, the degraded parts became clearer.

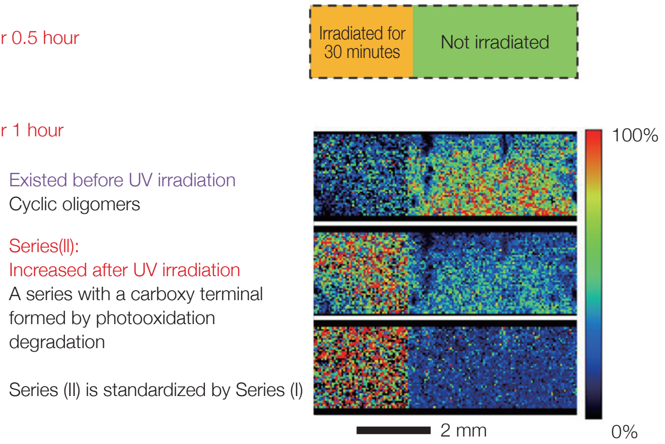


Time of UV irradiation



Series of oligomers formed by UV irradiation

Time of UV irradiation



Existed before UV irradiation
Cyclic oligomers

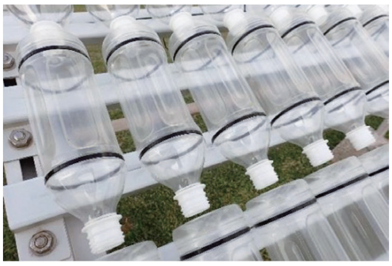
Series(II):
Increased after UV irradiation
A series with a carboxy terminal formed by photooxidation degradation

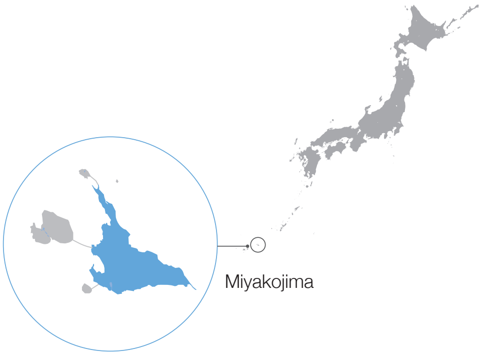
Series (II) is standardized by Series (I)

2-3 Analysis of PET Bottles for Outdoor Exposure Testing

Test method

Conforms to JIS Z 2381 (General Requirements for Atmospheric Exposure Testing)
Type of test: Direct exposure
Exposure angle: 20 degrees south face
Place of testing: Miyakojima, Okinawa
Sampling period: 0.5, 1, and 2 years
Start date: November 2020



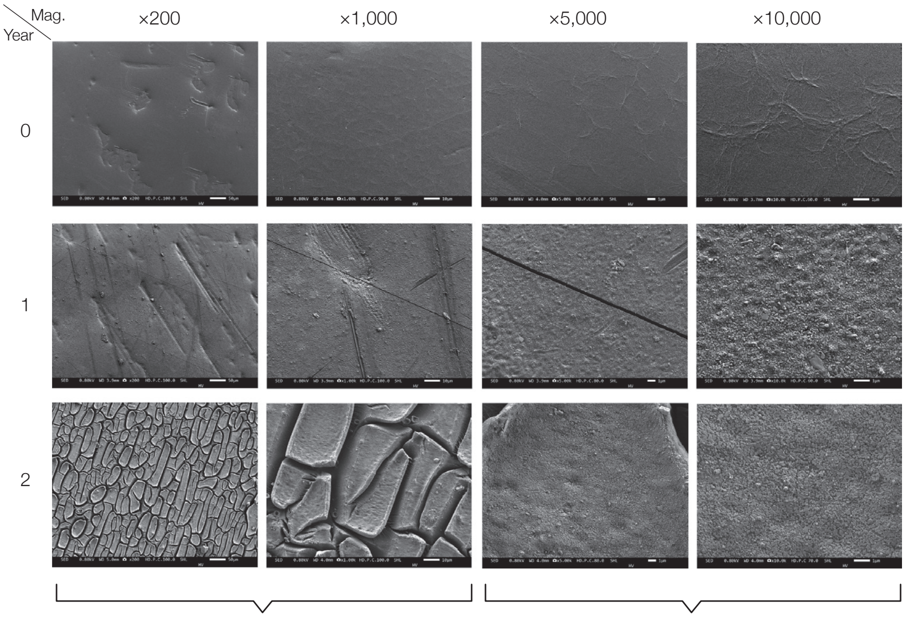


Acknowledgements: Samples were provided by courtesy of the Council for PET Bottle Recycling for the degradation evaluation of PET bottles through outdoor exposure testing.

Morphological Observation of PET Surface Using SEM

By using SEM, new PET surfaces and surfaces exposed to outdoor atmosphere for 1 and 2 years were observed at various magnifications. Since SEM uses electron beams as the irradiation source, the influence of charge must be considered when observing highly insulating polymer surfaces. However, by observing at low incident voltage, the charge on the sample surface can be reduced, and the morphology of the polymer surface can be visualized without a conductive coating. In addition, by acquiring the secondary electron images of the surface, it is possible to obtain an image with a large focal depth, which is difficult to obtain with an optical microscope as well as observe the microstructure of the surface in detail.

Sample: Surface of PET film
(without a conductive coating)

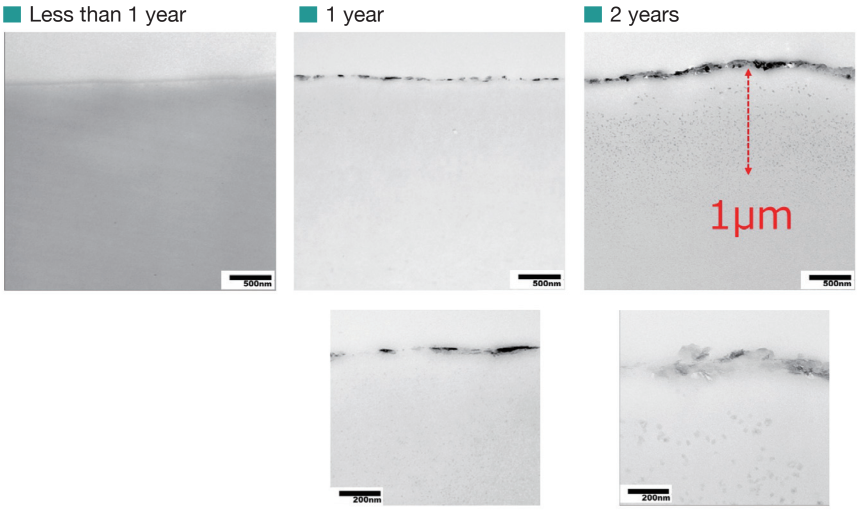


Degradation verified in the order of µm

Degradation verified in the order of hundreds of nm

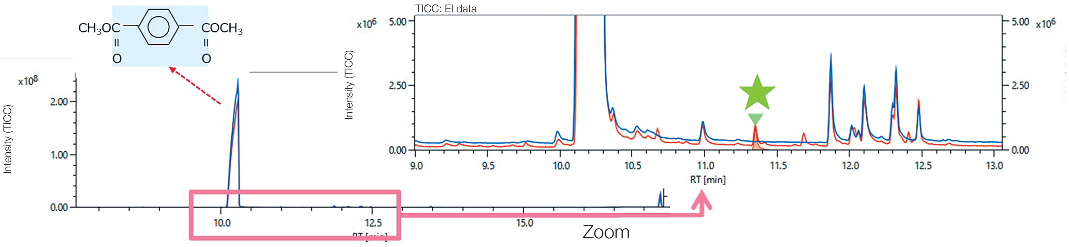
Cross Section Observation by TEM

The cross section near the sample surface was observed using a transmission electron microscope. The result showed that structural changes appeared at a depth of 1 µm on the sample surface with the age of the outdoor exposure testing.

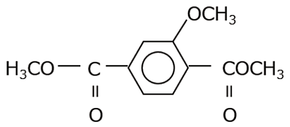


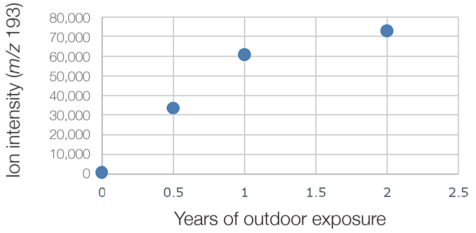
Degradation Analysis by Reactive Pyrolysis GC-MS

The components, which are reaction pyrolysis products derived from the PET main chain were strongly detected. These were common components before and after UV irradiation. As a result of the difference analysis of the outdoor exposure test between 0 year and 2 years, a component characteristic of the outdoor exposure test was observed at a retention time of 11.37 minutes in the total ion current chromatogram (TICC). The components of the peak that increased from the outdoor exposure test were the same as those which increased due to UV irradiation onto the PET film described on page 36. An EIC was created at the base peak of component ★ to confirm the change of area value with respect to UV irradiation time (average value of n = 3).
As a result, it was found that there was a rapid increase within one year of outdoor exposure, and the increase rate became gradual after that.



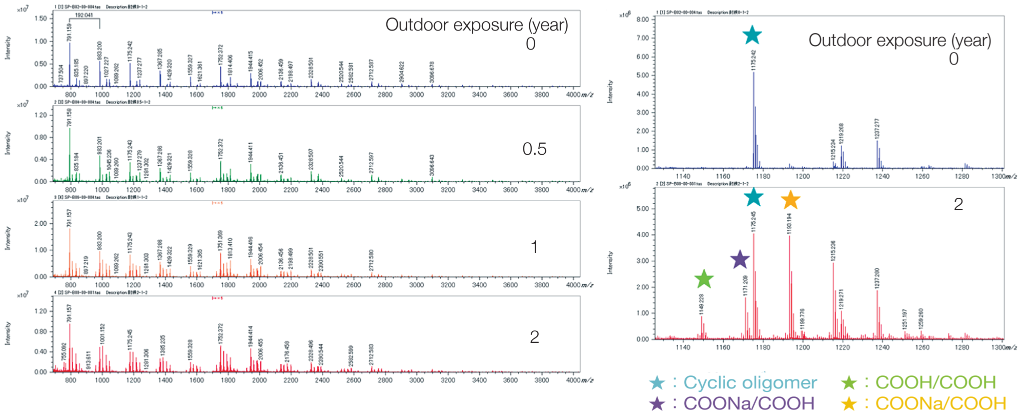
Estimated structural formula for ★



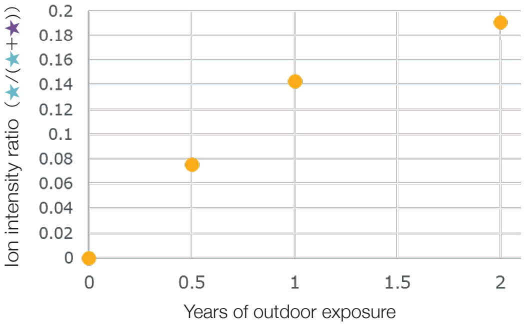

Note: EIC creation conditions: *m/z* 193.050, *m/z* depth: ±0.05 Da

Degradation Analysis by MALDI-TOFMS

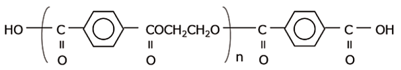
Before the outdoor exposure testing, a series derived from the cyclic oligomer of PET was mainly observed. After the outdoor exposure testing, the series COOX/COOX terminus (X = H, Na), which was presumed to have carboxy terminus derived from the photooxidation reaction, was observed. These were identical to the series observed by UV irradiation onto PET reported on page 36. When the ion intensity ratio of the series with the cyclic oligomer and the carboxy terminal was determined, the carboxy terminal series increased. It was found that the rate of increase during the second year was less than that of the first year.



All observed ions are [M+Na]⁺



Estimated structure of the series formed by UV irradiation



JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. 81-3-6262-3561 Fax. 81-3-6262-3577
www.jeol.com ISO 9001 • ISO 14001 Certified

▼ Local office

• AUSTRALIA & NEW ZEALAND • BELGIUM • BRAZIL • CANADA • CHINA • EGYPT • FRANCE • GERMANY • UNITED KINGDOM (UK) • INDIA • ITALY • KOREA • MALAYSIA • MEXICO • RUSSIA
• SWEDEN • SINGAPORE • TAIWAN • THAILAND • THE NETHERLANDS • UNITED ARAB EMIRATES (UAE) • UNITED STATES OF AMERICA (USA)

No.0104B559C(Bn)