Investigation of Synthetic Polymer Characterization by means of SEC/ESIMS

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It is difficult to analyze synthetic polymers using mass spectrometry, because they have a very wide molecular distribution (Mw/Mn). But if we select a relatively low molecular species, we can obtain information on polymer structure by means of MS. In this paper we describe an analysis method for synthetic polymers by means of SEC/ESIMS (using q-MS), some analysis cases, and the problems of this method.

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Introduction

For mass spectrometry of synthetic polymers, MALDI/TOFMS[1] is commonly used for general purposes due to its simplicity. Although a matrix is used as an ionization aid in the MALDI method, some trial and error is necessary to apply the method to the analysis of synthetic polymers and synthetic polymer compounds having unknown structures, as an appropriate matrix suitable for the target chemical substance(s) must be carefully selected. Furthermore, samples having large molecular weight distributions (Mw/Mn) are not readily ionized, and such samples require pretreatment refining. Therefore, in the MALDI method, it is necessary as a principle to combine with a separate fractionation system because online combination with chromatography is difficult.[2]

On the other hand, the ESI method [3], [4] is an effective ionization method for chemical substances having high ionicity or polarity. Through this method, hydrophobic synthetic polymers can also be ionized by using an alkali metal salt or other similar substances as a cationization agent, thus enabling a mass spectrum to be obtained.[5] Moreover, online combination with chromatography can be readily conducted in this method because ionization is performed by spraying a sample solution. This ionization method is most commonly used in the LC/MS method. Therefore, some structural analyses using SEC/ESIMS were reported in the early 1990s.[6] However, at the present time, the SEC/ESIMS method is not as commonly used as the MALDI/TOFMS method for general purposes because high performance systems having high mass resolution are required for analyzing complex and detailed mass spectra.

Although few reports exist on the SEC/ESIMS method utilizing quadrupole mass spectrometers (q-MS) having low mass resolution [7], important information such as molecular weight and constitutional repeating units, which are required for structural analyses of synthetic polymers, should be obtained if limiting the analysis targets to components having relatively low molecular weights (up to around 10,000). In this paper, we will explain what level of analysis can be achieved using a q-MS by introducing spectrum analysis methods and measurement procedures.

Furthermore, this paper consists of revised versions of the reports released at the 54th Annual Conference on Mass Spectrometry Osaka Japan 2006 and at a workshop for mass spectrometry entitled “Recent development of synthetic polymer analysis” [8] and the 9th and 11th National Symposium on Polymer Analysis and Characterization [9], [10]. The progress of systems and methods in the field of synthetic polymer mass spectrometry is extremely rapid. Please refer to the latest data and documents for the current situation.

Information on SEC/ESIMS

SEC (size exclusion chromatography) is a liquid chromatography technique which separates sample substances according to their molecular sizes. It elutes substances having larger molecular sizes faster than those with smaller sizes. It is more commonly referred to as GPC (gel permeation chromatography). However, in this paper, we will refer to this method as SEC because this expresses its separation principle.

In the SEC/ESIMS method, SEC and ESIMS are combined online [6), 7)]. **Fig. 1** shows a block diagram of the system used for the investigation that we conducted in this case. For the cationization agent, the post column addition method --in which the agent is added after the column is eluted-- was used.

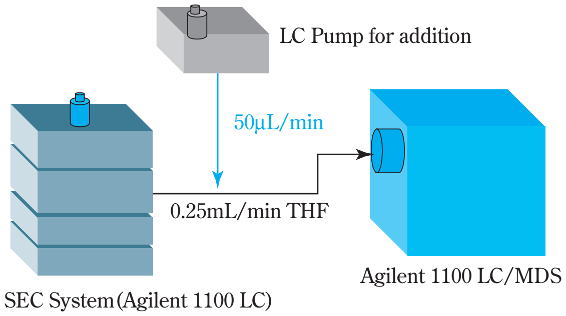


Fig. 1 Schematic Diagram of SEC/ESIMS System

Evaluating Cationization Agents

In the SEC analysis of hydrophobic synthetic polymers, THF (tetrahydrofuran) and chloroform are commonly used for the mobile phase. For the cationization agent, NaI and KI are commonly used due to their solubility in the mobile phase.[5)] In order to obtain a cationization agent that can also substantially ionize macromolecular components, we compared KCl, NaI and KI. The cationization agent was a 1:1 mixed solvent of water and acetonitrile at a concentration of 1mM. The mixed solvent was then added at a rate of 0.05mL/min using the post column addition method. The samples used for the evaluation were mixtures of different molecular weights of PMAA (poly-methylmethacrylate, **Fig. 2**) from Polymer Laboratories, Inc., which was commercially available as a molecular weight calibration reference standard,The molecular weights (MW) used for mixing were 3100, 6540, 9400, 12700 and 29300. The concentration was 1mg/mL and the injection rate was 25μL.

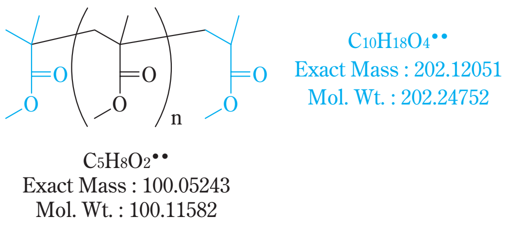
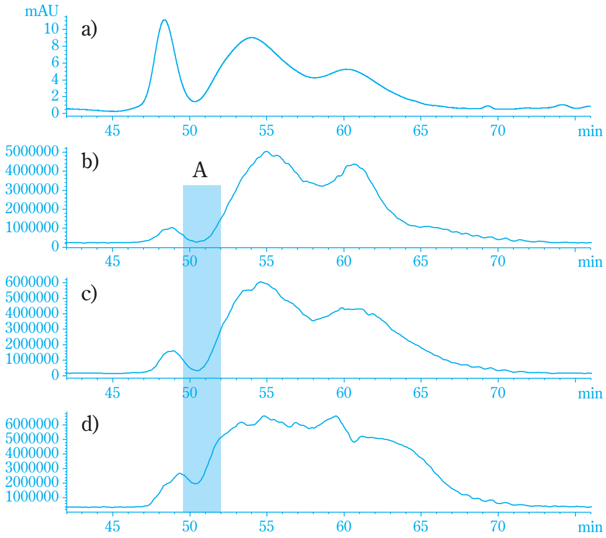


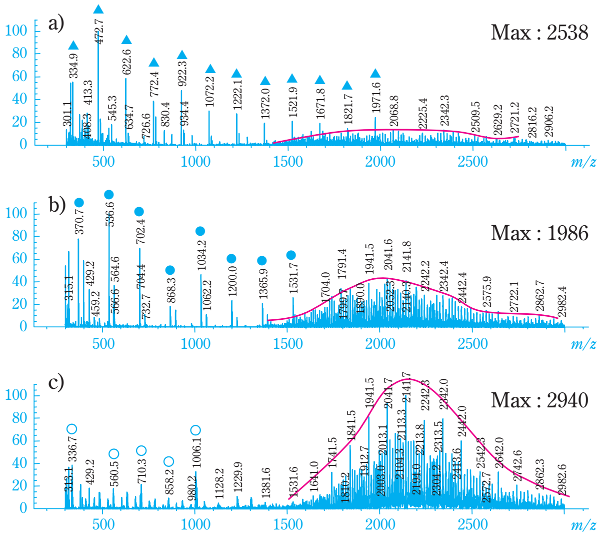
Fig. 2 PMMA (Poly-methylmethacrylate)

Fig. 3 shows the chromatogram and **Fig. 4** shows the mass spectrum in the area A (with no background processing).



a) 220nm. b) TIC, +NaI. c) TIC, +KI. d) TIC, +KCl
A ; averaging area of spectrums in Fig. 4
Column ; Tsk-gel Super HZ (4000*3+3000+2500*2)

Fig. 3 Size-exclusion Chromatograms of PMMA mixture



a) +NaI. b) +KI. c) +KCl

Fig. 4 SEC/ESIMS Spectrum at A

As a result, although there was no large difference observed in TIC (total ion chromatogram), substantial differences were observed in the mass spectra. For NaI, a group of cluster peaks (▲) caused by NaI and with intervals of 150Da was detected more strongly than the PMMA peak (indicated with a solid red line), which was considered to be the background spectrum. For KI, a group of cluster peaks (●) caused by KI and with intervals of 166Da was detected more strongly than the PMMA peak.

Conversely, for KCl, the background peaks were weak (○) and the PMMA spectrum was detected as the primary peak group. It was clear that the anionic part of the cationization agent greatly affected the background spectrum, thus influencing the ionization of the analysis target.

On the metal surface of the ESI probe tip, to which a high voltage was applied, it can be assumed that the following reaction with anions occurs: since Cl_2 has higher volatility than I_2, it can be more readily discharged outside the system (outside the mobile phase), thus producing only a minimal amount of cluster ions. Therefore, it is assumed that the sample itself can be more readily ionized.

$$2Cl^- - 2e^- \longrightarrow Cl_2 \qquad 2I^- - 2e^- \longrightarrow I_2$$

As a result of our investigation --we will not describe the details here--, it has been clarified that both KCl and KOH show the highest sensitivity to high-molecular-weight components and produce simpler spectra.

SEC/ESIMS Spectra of Synthetic Polymers

In general, when measuring high-molecular-weight components using the ESI/MS method, an MS spectrum with multiply-charged ions can be obtained.[11] In the SEC/ESIMS spectra of hydrophobic synthetic polymers when using a cationization agent, multiply-charged ions to which several cationization agents are added can be detected. In order to estimate the molecular weight of the target substance based on the SEC/ESIMS spectra, it is necessary to analyze the peaks of these multiply-charged ions.

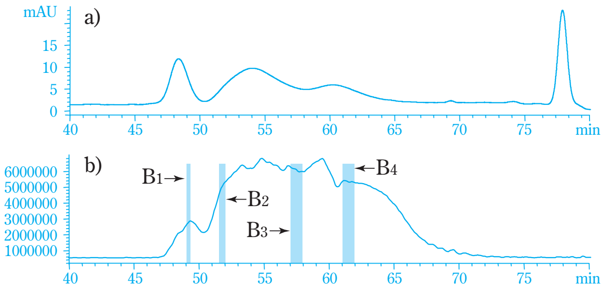
When considering the PMMA molecule as M, and measuring it in a positive ion mode using KCl as the cationization agent, the PMMA becomes ionized in the form $[M+zK]^{z+}$. z indicates the charge number. In this case, it is equivalent to the number of K^+ ions added when the molecular weight is rather small, $z=1$. However, when the molecular weight is large, it is detected as multiply-charged ions in which $z \geq 2$.

The threshold at which multiply-charged ions appear differs depending on the type of chemical and cationization agent. In the case of PMMA, divalent ions begin to appear once n=20 and the molecular weight is approximately 2000 (Fig. 2). As the molecular weight increases, the number of charge numbers detected increases to trivalent and further to tetravalent. In addition, these can be detected in the form of a sequence of peaks, such as divalent, trivalent and tetravalent. **Figs. 5** and **6** show the actual measurement results.

As shown in Fig. 6, an ESIMS spectrum that does not use SEC appears to be a single sheet diagram in which all the spectra shown in the graphs B_1–B_4 are overlaid. For this reason, it is generally considered that multiply-charged ion spectra are complex and hard to analyze.

However, when using SEC, the samples are measured in order of their molecular weights, thus enabling the overlaid multiply-charged ions to become separated from each other. As a result, the spectrum becomes simpler, thus leading to easier analysis. However, as shown in B_1, it is still difficult to conduct SEC analysis of high molecular weight areas having low separation capability. On the other hand, this can also be evidence that PMMA is ionized. Therefore, it can be considered that once the separation capability of SEC is improved, molecular weight estimation of high-molecular-weight components will be possible.

The x-axis of a mass spectrum is m/z (mass-to-charge ratio). m indicates the molecular weight of the detected ion, and z indicates the charge number



a) 220nm b) TIC, 1mM KCl +0.05mL/min
B_1~B_4 ; averaging area of each mass spectrum in Fig.6
B_1 ; 49.0 – 49.2min B_2 ; 51.5–52.0min B_3 ; 57.0 – 58.0min
B_4 ; 61.0 – 62.0
Column ; Tsk-gel Super HZ (4000*3+3000+2500*2)

Fig. 5 Size-exclusion Chromatograms of PMMA mixture

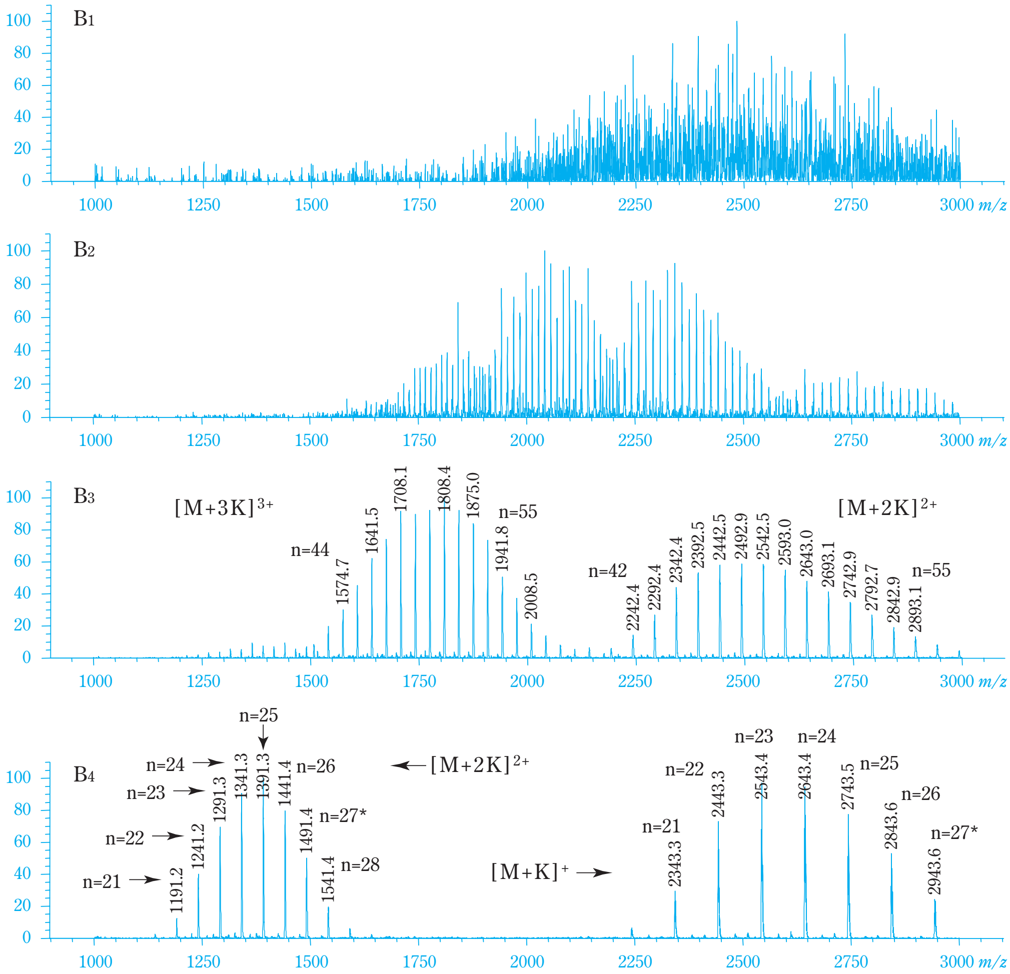


Fig. 6 SEC/ESIMS (+KCl) Spectrums at B1 to B4

(=charge state) as described previously.

In Fig. 6, we examined a PMMA molecule with n=55 (molecular weight 5708.6). The molecular weights of the K+-added divalent and trivalent ions are shown below. The molecular weight was used for the calculation, not the precise mass:

$5708.6 + 2 \times 39.1 = 5786.8$ ------ $[M+2K]^+$

$5708.6 + 3 \times 39.1 = 5825.9$ ------ $[M+3K]^+$

However, as the mass spectrum is detected using the mass-to-charge ratio (m/z), peaks are detected at the positions of 2893.4 $[M+2K]^+$ and 1942.0 $[M+3K]^+$. The measured values shown in Fig. 6 are quite consistent with the values obtained by the calculation.

Thus, in order to estimate the molecular weight from the multiply-charged ion spectra (peaks), the charge number must be determined. However, when measuring macromolecules having completely unknown structures, the charge number must be determined from the spectrum only.

Determining Charge Number Using Isotope Peaks

Generally, charge numbers are determined by the peak intervals between isotopes. **Fig. 7** shows enlarged $[M+K]^+$ and $[M+2K]^{2+}$ peaks of PMMA (n=27). The mass spectrum peaks indicate the distribution of stable isotopes corresponding to the numbers and types of elements contained in the detected chemical compound. As shown in a) of Fig. 7, several peaks appear, showing a pattern which reflects the isotope distribution (abundance ratio). When measuring a 1+ charged ion (i.e., z=1), the interval of these peaks (m/z interval) is inversely proportional to the atomic mass unit (1Da). Therefore, for a 2+ charged ion (z=2), the atomic mass unit is 0.5Da; for a 3+ charged ion, the unit is 1/3Da=0.333…; and for a tetravalent ion 4+ charged ion, the unit is 0.25Da. However, as shown in b) of Fig. 7, because a spectrum measured using a q-MS having low mass resolution does not possess adequate mass resolution capability, even the 2+ charged ions cannot

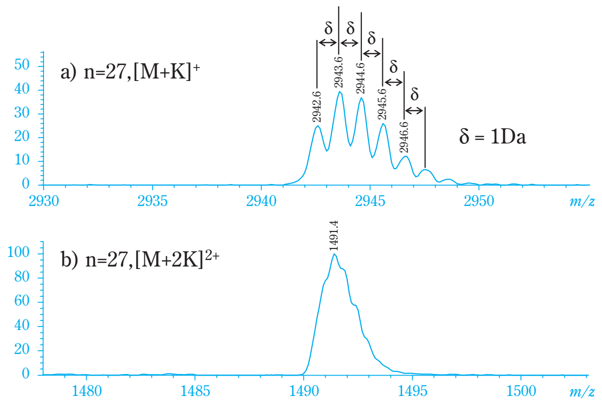


Fig. 7 Profile Spectrum of n=27 peak (see Fig.6)

be determined. In b) of Fig. 7, the resolution is approximately 2,000 (FWHM). Therefore, in order to measure the molecular weight of synthetic polymers using the SEC/ESIMS method, it is necessary to use a high resolution mass spectrometer, such as TOFMS or TF-MS.[12]

Fig. 8 shows the mass spectra of the same sample containing the same components, but measured using a quadrupole time-of –flight (q-TOF) mass spectrometer (q-tof Ultima of Micromass Ltd.). Although the details of the measurement conditions are omitted here, the mass resolution is approximately 6,000 (FWHM) for actual measurements. As the diagram clearly shows, it is easy to determine 2+ charged ions. However, even at a resolution of 6,000, 3+ charged ions cannot be determined. Since the resolution of a standard q-TOF mass spectrometer is approximately 10,000 (FWHM) even with precise adjustment, when using isotope peak intervals, the charge numbers can be determined only up to 4 at m/z=2,000, and up to 2 at m/z=4,000. Thus, it is necessary to use FT-MS with higher resolution or find other methods.

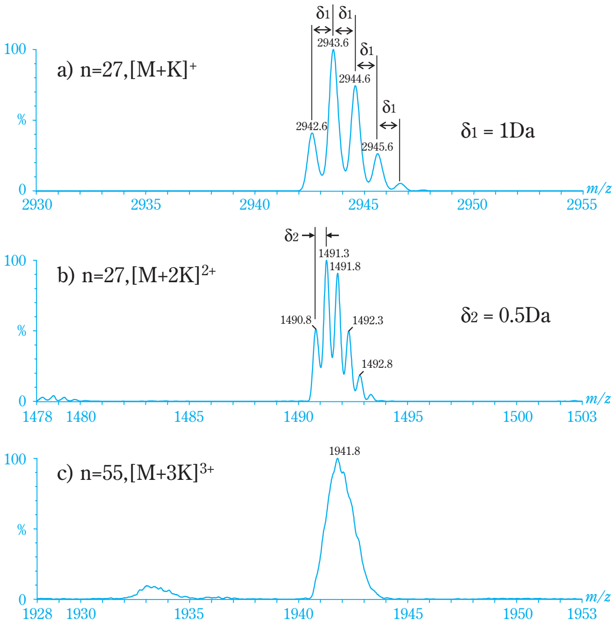


Fig. 8 High resolution SEC/ESIMS Spectrum resolution = 6000(FWHM)

Estimating Charge Number Using Molecular Weights of Constitutional Repeating Units

Fig. 9 shows an enlarged view of spectrum B_2 (Fig. 6). In spectrum B_2, the peaks are aligned from the low m/z side (the left side) in the order of the higher charge number 5,4,3 and 2. At this stage, because the charge numbers of each peak is still unknown, they are represented as $+(z+1)\mathrm{K}$, $+z\mathrm{K}$, $+(z-1)\mathrm{K}$. a) and b) show enlarged spectra of the parts indicated by the dotted lines. Because there is not adequate mass resolution, the isotopic peak intervals cannot be read. The figures indicate the intervals between the peaks x1 to x8 and those between the peaks y1 to y6. These intervals are derived from the constitutional repeating unit (CRU) of PMMA. Therefore, they match the molecular weight in the CRU, and when measuring a 1+ charged ion, the value is 100Da. However, as multiply charged ions are being measured in the diagram, the values are smaller than 100Da. In the previous section, it was explained that the detected m/z value decreases as the charge number increases, but in the same way, smaller molecular weights are also detected in the CRU -- such as

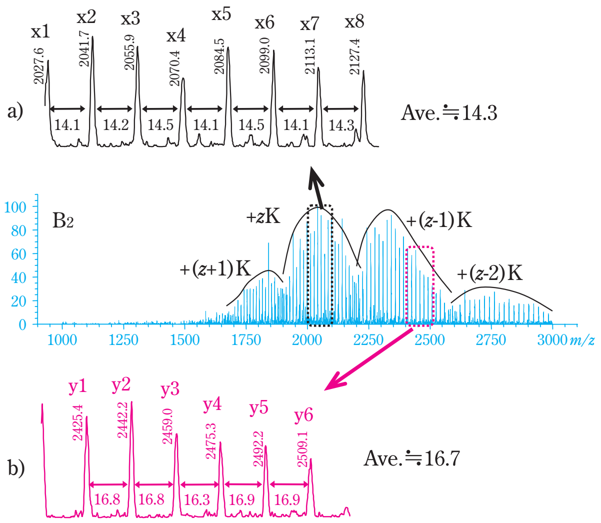


Fig. 9 Expanded Spectrum A2
$14.3 \times 7 = 100.1$ $16.7 \times 6 = 100.2$ $z = 7$

1/2, 1/3 and so on -- as the detected charge number increases. The reason why the intervals on the high molecular weight side shown in a) are greater than those on the low molecular weight side shown in b) is because each peak on the high molecular weight side in b) is one charge number smaller than that on the low molecular weight side in a). The average of the $+z$K peak intervals is 14.3 and that of the $+(z\text{-}1)$K peak intervals is 16.7. As charge numbers of these peaks are equivalent to z and z-1, the following equation can be established:

$$z \times 14.3 \approx (z\text{-}1) \times 16.7$$

As this contains inaccuracies, it cannot be strictly "=." However, if making z=7, the following equations can be obtained:

$$7 \times 14.3 = 100.1 \qquad 6 \times 16.7 = 100.2$$

Therefore, the charge number and molecular weight in the CRU can be estimated. In this case, the molecular weight in the CRU can be estimated as 100, and this is certainly consistent with PMMA.

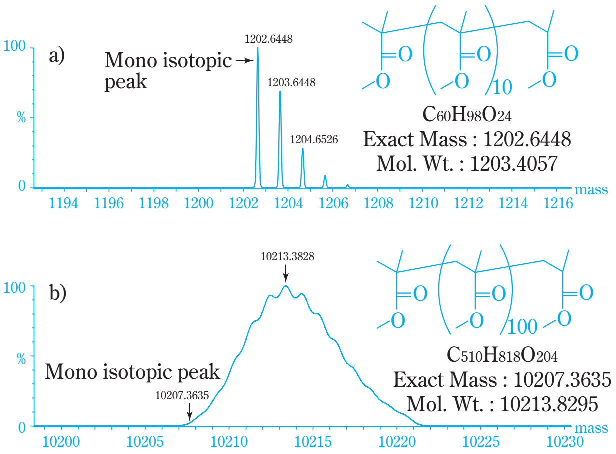
Naturally, because this method can be applied only to cases in which the selected peaks are those of the same kind of synthetic polymer, it is necessary to take extra caution when applying the method to mixed polymers. From our experience however, it can be said that this molecular weight estimation method is highly effective in many situations.

Mass Spectra and Molecular Weights of Components Having High Molecular Weights

Once the charge number has been determined, the molecular weight can be readily estimated. However, when comparing with theoretical values, mass spectra of components with high molecular weights have further problems.

Fig. 10 shows the simulation results of M+ mass spectra of 10-mer a) and 100-mer b) of PMMA. The mass resolution is 10,000 (FWHM). However, it should be noted that it is not strictly M+, as electron mass is not taken into account. (10-mer and 100-mer refer to the value "n" described in Fig. 2.)

As previously mentioned, the mass spectrum reflects the abundance ratios of stable isotopes. Because the molecular weight of the 10-mer is approximately 1,000 and the mass resolution is 10,000, the half-value width of the isotopic peak is around 0.1Da. Therefore, adequate separation and extremely sharp peaks can be achieved. However, peaks on the low molecular weight side are produced by molecules composed of a single isotope, and are called a mono-isotopic peaks. The value of such peaks is equivalent to the exact mass, and is used when conducting accurate mass measurements. Roughly speaking, this exact mass can be used for estimating low molecular weight components with molecular weights of up to approximately 2,000.



a) 10-mer b) 100-mer

Fig. 10 Simulated PMMA oligomer Peak (M^+) resolution = 10000 (FWHM)

However, as the molecular weight approaches 10,000 in the 100-mer, the appearance of the spectrum suddenly changes. Even though the mass resolution is 10,000, the molecular weight is also 10,000. Therefore, the half-value width of each isotopic peak becomes 1Da, thus allowing the peak width to expand to 10 times wider than that of the 10-mer. Also, because the number of atoms constituting the molecule is large, there are more varieties of isotope combinations, thus increasing the number of peaks. For this reason, as shown in b) of Fig. 10, each isotopic peak can be barely separated, thus shaping the peak like a broad mountain. In addition, as the mono-isotopic peak appears at the foot of this broad peak, its peak cannot be identified. In other words, unless precise observation is conducted to define which area of the peak is considered as the molecular weight of the 100-mer, the molecular weights obtained from the experiment cannot be accurately compared. Although it is reasonable to regard 10213.3828 at the peak top as the molecular weight measured using MS, because this value differs from the molecular weight (MW), when measuring and evaluating the molecular weight of a component having high molecular weight using a mass spectrometer, it is necessary to confirm the detected molecular weight through the spectrum simulation method introduced here. In this paper, the value at the peak top of the simulation spectrum was used as the theoretical molecular weight and then compared to the actual measured value using MS.

Accuracy of Molecular Weight Estimation Using Multiply-charged Ion Peaks

Table 1 shows the results of estimates of the molecular weights of the x5 and y5 components shown in Fig. 9. In the calculated values, MW represents molecular weights, which are shown for reference purposes. Using a q-MS, components having molecular weights of 14,000 or more were estimated from +6K and +7K ions. As a result, it has been confirmed that the error is within ±1Da. Therefore, the error is within 100ppm, meaning an accuracy of ±0.1 in the *m/z*=1,000 conversion. This is extremely good consistency, and we therefore believe that this method can be used for structural analysis of actual synthetic polymers. According to our investigation, molecular weights of up to approximately 18,000 can be accurately estimated with +8K ions when using PMMA.

Table 1 PMMA MW from SEC/ESIMS Spectrum

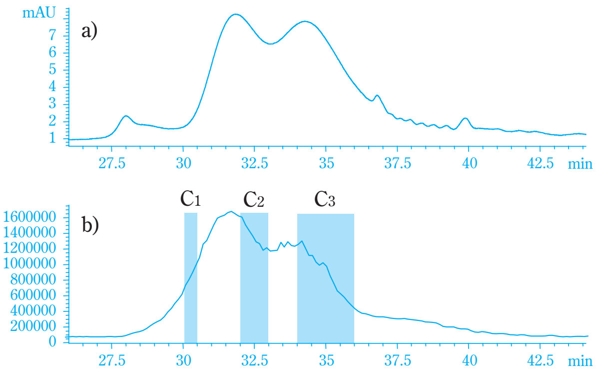
Peak (*m/z*)	ion type	Experimental MW	Calculated	
			Peak top	MW
2084.5	M+7K	14718.6	14718.7	14719.0
2492.2	M+6K	14317.8	14318.4	14318.6

For reference purposes, the *m/z* detection accuracy using a q-MS is usually ±0.1Da. For example, if the detection accuracy for 6+ charged ions is ±0.1Da, the error in the molecular weight obtained from the calculation becomes ±0.6Da. Therefore, theoretically, the accuracy of molecular weight estimation from multiply charged ions using a q-MS is acceptable. If the *m/z* detection accuracy is improved by one order of magnitude, to approximately ±0.01Da, we believe that the accuracy of molecular weight determination for synthetic polymers will greatly improve, thus enabling more detailed structural analysis by using a combination of a q-MS and SEC/ESIMS.

Synthetic Polymer Mixtures

Figs. 11–13 show the measurement results of a PPG/PMMA mixture. Needless to say, these two components cannot be distinguished using a UV chromatogram or TIC, neither can the presence of the two components be presumed. Although precisely analyzing each peak using the spectra shown in Fig. 12 may indicate that it is a PPG/PMMA mixture, it requires time, effort and creativity. When only using an MS spectrum for analysis, as soon as samples become mixtures, analysis becomes extremely difficult.

Therefore, we attempted the analysis via a two-dimension plot (Fig. 13). In the diagram, the data obtained from the SEC/ESIMS measurement are



a) UV=220nm b) TIC(+KCl)
C_1~C_3 ; averaging area of the mass spectrum in Fig.12
Column ; Tsk-gel Super HZ (2500+2000*2+1000)

Fig. 11 Size-exclusion Chromatograms of PMMA+PPG

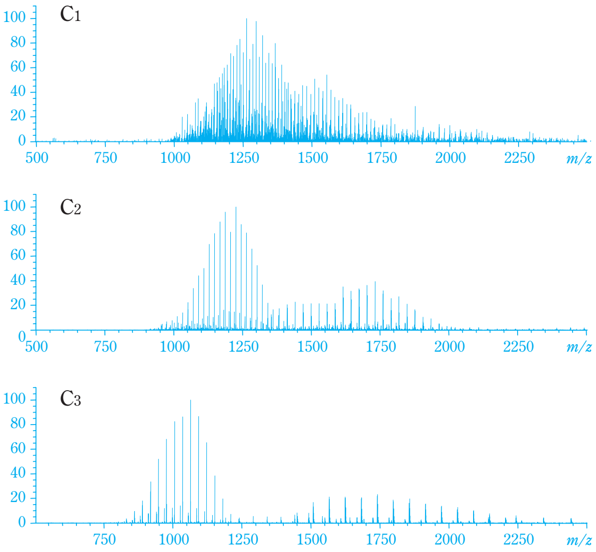
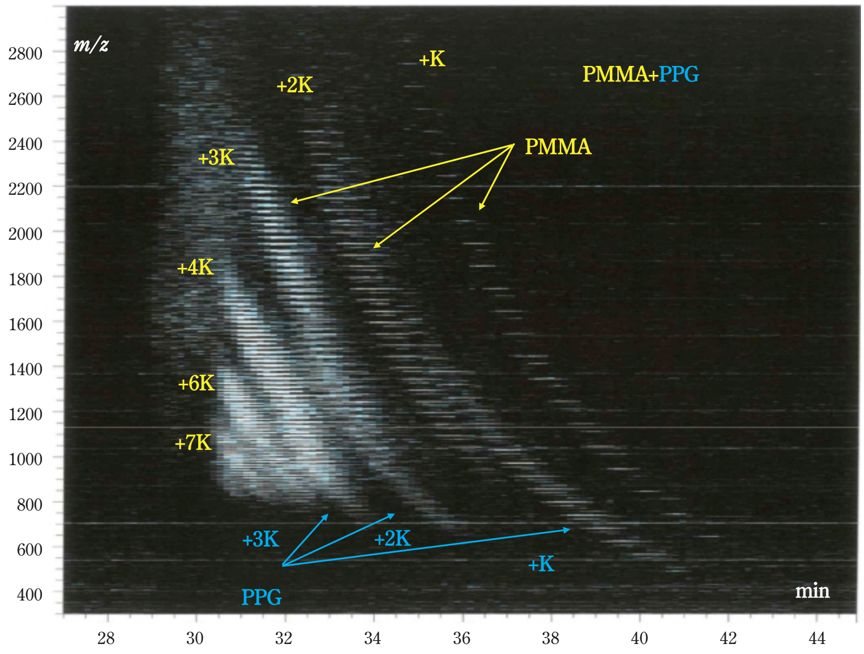


Fig. 12 SEC/ESIMS(+KCl) Spectrum at C_1~C_3
Sample ; PMMA+PPG



Column ; Tsk-gel Super HZ (2500+2000*2+1000)

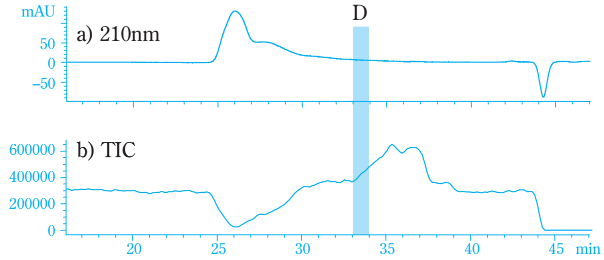
Fig. 13 2-D Plots of SEC/ESIMS of PMMA+PPG

expressed as follows: the vertical axis represents *m/z*; the horizontal axis represents dissolution time (minutes); and the intensity gradation represents the strength of each ion peak. The presence of the two components can be presumed at a glance. Analyzing the mass spectrum based on this information, it is clear which peak groups correspond to PPG, and which to PMMA, from among the components. In addition, with respect to charge state, even the charge state of high molecular weight components having complex mass spectra (and therefore being difficult to have their charge state determined) can be estimated from the elution behavior of each component. From Fig. 13, it can be observed that the separation of high molecular weight components is not adequate when using SEC. Furthermore, it can be readily understood that in order to analyze high molecular weight components more precisely, improving the separation capability can be effective by increasing the number of columns, and by other methods.

Thus, it is obvious that 2-D plots are extremely effective in order to analyze synthetic polymers having complex compositions, as well as mixtures.

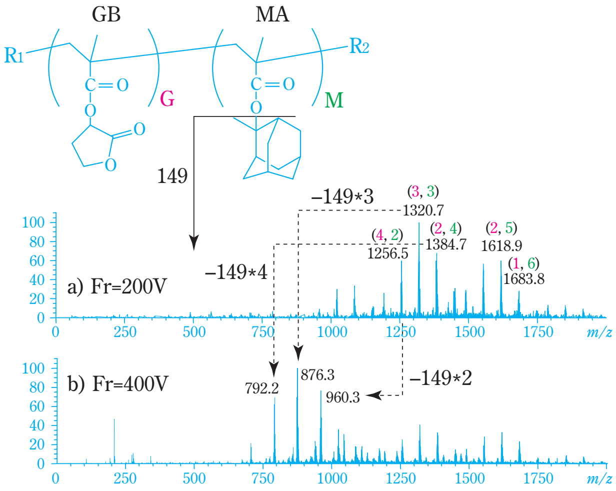
GB/MA Copolymer

Figs. 14–16 show the measurement results of a GB/MA copolymer, which is a more practical sample.



a) 210nm b) TIC of SEC/ESIMS
D ; averaging area of mass spectrums in Fig.15
Column ; Tsk-gel Super HZ (2500+2000*2+1000)

Fig. 14 SEC of GB/MA copolymer



a) Fragment Voltage=200V b) Fragment Voltage=400V

Fig. 15 GB/MA copolymer SEC/ESIMS Spectrums at D

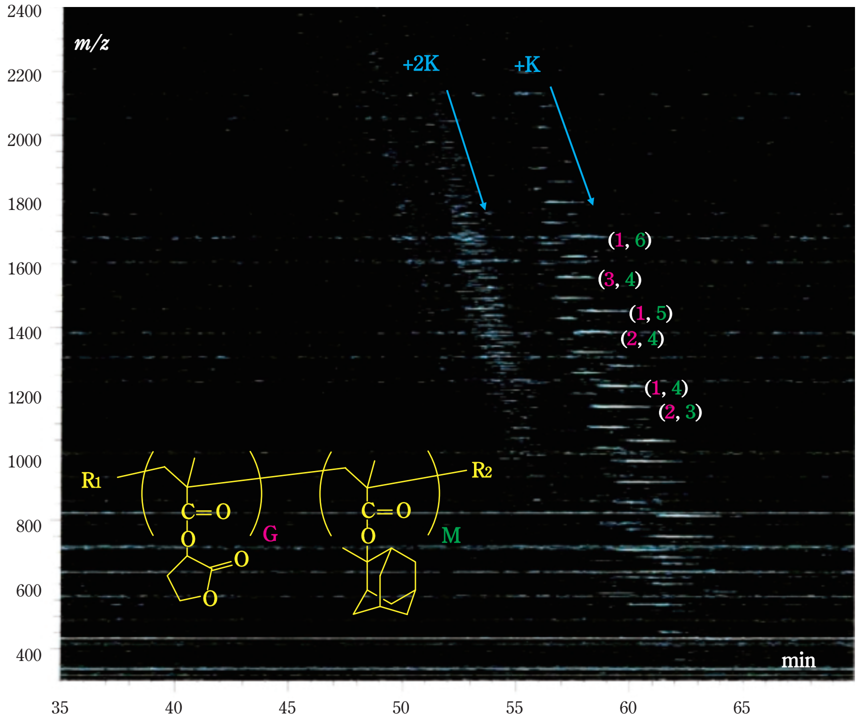
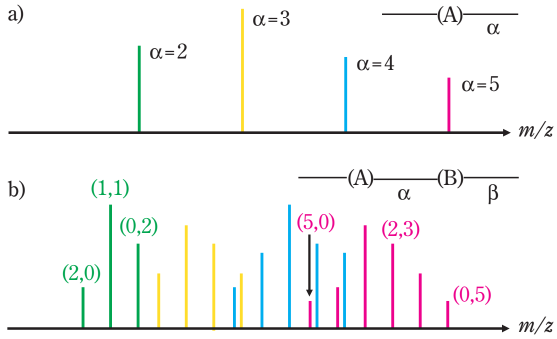


Fig. 16 GB/MA copolymer 2–D plot by SEC/ESIMS (1,6) means G=1, M=6

This sample was synthesized by radical polymerization. The weight-average molecular weight (Mw) is ≈ 10,000 and the distribution (Mw/Mn) is ≈ 1.9 (indicated as polystyrene). Although the Mw is rather small, the sample has a wide Mw/Mn and a random sequence, thus making its composition extremely complex. For this reason, with ESIMS measurement using the flow injection method that does not utilize SEC, it was difficult to determine whether or not the sample had been ionized because the spectrum was extremely complicated.

With the SEC/ESIMS (+KCl) method, the mass spectrum that reflects the copolymer composition was detected as a $[M+K]^+$, thus making it easy to estimate the molecular weight for low molecular weight components (up to approximately MW=2,500). As a result, the composition of each peak could be identified (Fig. 15, a)). It was also understood that more precise information can be obtained through the capillary skimmer CID method (Fig. 15, b)).

In addition, it was understood that information regarding dissolution behavior and charge state, which is useful for analyzing mass spectra, can be obtained from 2-D plots (Fig. 16). In the 2-D plot, it was also clearly confirmed that a 2+ charged ion that could not have been identified in a regular mass spectrum was also detected. However, because the spectrum of this 2+ charged ion was extremely complex, it was difficult to specify the components and estimate the molecular weight.



a) homo-polymer model b) co-polymer model
α, β=1,2,3···, (2,3) means α=2, β=3

Fig. 17 Complexity of copolymer mass spectrum

Fig. 17 shows the complexity of the mass spectrum of a copolymer. We believe that from this model spectrum, it can be observed that although it is a mere A/B copolymer, its mass spectrum can become unimaginably complex. In order to analyze a complex copolymer which has several (>3) kinds of constitutional repeating unit, it is essential to use chromatography which has high separation capability.

Conclusion

From the results described above, the following fact has been confirmed: although hydrophobic synthetic polymers can be ionized up to molecular weights of tens of thousands by the SEC/ESIMS method using a cationization agent, if the composition of the polymer is complex, it is hard to estimate its molecular weight. Therefore, it can be concluded that in order to conduct structural analysis of a synthetic polymer, it is more important to use chromatography which has high separation capability, rather than a high performance mass spectrometer.

Furthermore, using the PMMA in Fig. 2 as an example, when analyzing the molecular weight of the CRU, if only n=100 compounds are extracted, refined and measured, only the molecular weight of the n=100 compounds can be clarified, not that of the CRU. In order to obtain the molecular weight of the CRU, a group having consecutive numbers such as n = ---- 98, 99, 100 --- must be analyzed. Such groups cannot be analyzed using UV or TIC, but the 2-D plots shown in Figs. 13 and 15 are effective. We believe that if there is a function which can plot only the trivalent ion spectrum directly from a 2-D plot, and which can conduct background processing, mass spectra which are easier to analyze can be achieved, resulting in more efficient and precise analysis.

In recent years, there have been some reports on new software for copolymer composition analysis.13) Its development is expected to continue in the future.

Acknowledgements

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