A new experimental system has been developed, which enables measurements of linear as well as non-linear complex conductivities to be made. The frequency dependence of linear to fifth-order non-linear complex conductivities at different temperatures in a polyethylene oxide/salt complex can then be measured. A characteristic conduction relaxation phenomenon was observed in the spectra, which suggested the existence of different ion-conduction mechanisms between the high- and low-frequency regions. It was also found that the ratio of linear to non-linear conductivities was closely related to the elementary process of ionic transport. Furthermore, this ratio obtained from non-linear measurements allowed an estimate of the important parameters which characterized ionic transport in ion-conducting polymers, such as the hopping distance of an ion or the size of a connected cluster of the site capable of ion hopping, without the need for any additional assumptions. Thus, it was found that in a polyethylene oxide/salt complex, the typical size of a connected cluster of the effective sites capable of ion hopping was approximately 4 nm.

1. Introduction
In the past, studies on ion-conducting polymers have centred around polyethylene oxide and alkali metal salt complexes [1–6]. These studies were initiated by the series of studies conducted by Wright and co-workers in the 1970s, who found relatively high conductivity in the polyethylene oxide/salt complex [1–3]. Studies in this field were further promoted by the report of Armand [7] who indicated that the complex of polyethylene oxide and alkali metal salt, in particular lithium salt, was a lithium-ion conductive solid electrolyte, and that it could possibly be applied to solid-state batteries, for example. Various new ion-conducting polymers have been produced with the aim of actual utilization [1–7].

Polymers adsorbing low molecular weight compounds such as water have been known to show high ionic conductivity. In such polymers, the direct cause of high ionic conductivity, for example, dissociation and transfer of ions, depends on the type of low molecular weight compounds, and polymers themselves basically play the role of a matrix. In contrast, ion-conducting polymers are solids conducted by Wright and co-workers in the 1970s, who found relatively high conductivity in the polyethylene oxide/salt complex [1–3]. Studies in this field were further promoted by the report of Armand [7] who indicated that the complex of polyethylene oxide and alkali metal salt, in particular lithium salt, was a lithium-ion conductive solid electrolyte, and that it could possibly be applied to solid-state batteries, for example. Various new ion-conducting polymers have been produced with the aim of actual utilization [1–7].

The temperature dependence of d.c. conductivity, \( \sigma_{d.c.} \), in ion-conducting polymers [4, 5] is generally of the following Williams–Landel–Ferry (WLF) type [8]

\[
\log \frac{\sigma_{d.c.}(T)}{\sigma_{d.c.}(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}
\]

or Vogel–Tamman–Fulcher (VTF) type [9–11]

\[
\sigma_{d.c.}(T) = \frac{A_1}{T^{1/2}} e^{-\frac{T_0}{T - T_g}}
\]

where \( C_1, C_2, A_1, \) and \( A_2 \) are constants. \( T_g \) is the glass transition temperature, and \( T_0 \) is the temperature at which configuration entropy becomes zero. To explain this temperature dependence of the d.c. conductivity, the free-volume model [12] and its expansion, the configuration entropy model [13, 14], are often used. Assuming the cooperative nature of ionic transfer and local motion of polymer chains, the temperature dependence of mobility is calculated on the basis of local motion of polymer chains, and the temperature dependence of conductivity is presented based on this explanation [4–6, 14].

Detailed information regarding the correlation between ionic transport and dynamic behaviour of the polymer chain is expected to be obtained from the investigation of the frequency dependence of conductivity. In order to obtain useful information on this correlation, the frequency dependence of permittivity and conductivity in ion-conducting polymers was measured by many researchers [4, 5, 15–19]. However, although the above-mentioned free-volume model is effective in explaining d.c. conductivity because thermodynamics is introduced for the explanation of
static model to explain the frequency dependence of conductivity in ion-conducting polymers, the dynamic percolation model, was proposed by Ratner et al. [20] and Harrison and Zwanzig [21]. However, the dynamic percolation model is very complex, because it contains many physical constants in equations representing the frequency dependence of conductivity which cannot be determined experimentally. Therefore, in order to explain the frequency dependence of conductivity obtained by experiments, many assumptions must be made for the physical constants. Thus, although this model is theoretically established, complete verification of its validity by experiments is actually difficult to accomplish.

It has been noted that studies on non-linear spectra of conductivity may provide information regarding the elementary processes of ionic transport and formation of potential energy, which is difficult to obtain from measurements in the linear region. With respect to non-linearity of permittivity, pioneers Furukawa et al. [22] studied ferroelectric polymers. Referring to the methods used in their study, we have further advanced this field of research to develop a measurement system for non-linear conductive spectra. In this study, the newly developed measurement system was used to measure the temperature dependence of linear and non-linear complex conductive spectra in a polyethylene oxide/salt complex. The observed non-linear conductive spectrum exhibited a very complicated form including a relaxation phenomenon. By detailed analysis of these non-linear spectra, various parameters, such as non-linear d.c. conductivities and non-linear relaxation strength, were evaluated. Furthermore, the conduction mechanism of ions was studied using these evaluated parameters in an analytical method which took advantage of the characteristics of experiments on non-linear conductivity.

2. Experimental procedure

When the direct current, \( I_{d.c.} \), for a non-linear system is expanded in odd powers of the static electric field, \( E \)

\[
I_{d.c.} = \sigma_{1\,d.c.}E + \sigma_{3\,d.c.}E^3 + \sigma_{5\,d.c.}E^5 + \cdots (3)
\]

we can express the linear and non-linear conductivities in terms of coefficients of the exponents. Here \( \sigma_{1\,d.c.} \) is the linear d.c. conductivity. The coefficient \( \sigma_{n\,d.c.} \) for \( n \geq 3 \) defines the \( n \)-th order non-linear d.c. conductivity. However, when excitation is not a static field but a sinusoidal electric field, it is complicated in that complex non-linear conductivity is defined. On the other hand, complex non-linear permittivities have been already reported by Furukawa et al. [22].

For measurements of linear and non-linear conductivities, we applied a sinusoidal electric field

\[
E(t) = E_0 \cos \omega t
\]

with amplitude, \( E_0 \), and angular frequency, \( \omega \). If there exists a relaxation phenomenon in a sample, the response of electric current, \( I(t) \), is represented by

\[
I(t) = \sum_{n=1}^{\infty} \left( I'_{n} \cos n \omega t + I''_{n} \sin n \omega t \right)
\]

(5)

We have detected the in-phase and 90° out-of-phase components of the electric current, \( I(t) \), with frequency \( \omega_0 \). The phenomenological theory of stationary linear response is well established on the basis of Boltzmann's superposition principle. On the other hand, extending this theory of stationary linear response to a non-linear system, Nakada has developed a phenomenological theory of the non-linear relaxation response [23]. According to this theory, the resulting response can be expressed by a sum of convolution integrals of the applied electric field at multiple time points and the non-linear after-effect functions. When the excitation is given by Equation 4, the resulting response, \( I(t) \), is calculated as follows

\[
I(t) = [\sigma_1(\omega) \cos \omega t + \sigma_1'(\omega) \sin \omega t] E_0 + \\
[\sigma_3(3\omega) \cos 3\omega t + \sigma_3'(3\omega) \sin 3\omega t + \\
B_3(\omega) \cos \omega t + B_3'(\omega) \sin \omega t] E_0^3 + \\
\left[ \sigma_5(5\omega) \cos 5\omega t + \sigma_5'(5\omega) \sin 5\omega t + \cdots \right] E_0^5 + \cdots
\]

(6)

where \( \sigma_1(\omega) \) and \( \sigma_1'(\omega) \) are the real and imaginary parts of linear complex conductivity \( \sigma_1^*(\omega) = \sigma_1(\omega) + j\sigma_1'(\omega) \), respectively. \( \sigma_3(\omega) \) and \( \sigma_3'(\omega) \) are also the real and imaginary parts of \( 3 \)-th order non-linear complex conductivities \( \sigma_3^*(\omega) = \sigma_3(\omega) + j\sigma_3'(\omega) \), respectively.

Comparing Equations 6 and 5, we find relationships between the amplitude of the in-phase component, \( I'_{n} \), and the amplitude of the applied field, \( E_0 \), as follows

\[
I'_1 = \sigma'_1(\omega) E_0 + \frac{3}{4} \sigma'_3(\omega) E_0^3 + \cdots
\]

(7)

\[
I'_3 = \frac{1}{4} \sigma'_3(3\omega) E_0^3 + \frac{5}{16} \sigma'_3(3\omega) E_0^5 + \cdots
\]

(8)

\[
I'_5 = \frac{1}{16} \sigma'_5(5\omega) E_0^5 + \cdots
\]

(9)

Furthermore, the relationships between 90° out-of-phase components, \( I''_{n}(n = 1, 3, 5, \ldots) \), and \( E_0 \) are of the same forms as those of Equations 7–9, respectively

\[
I''_1 = \sigma''_1(\omega) E_0 + \frac{3}{4} \sigma''_3(\omega) E_0^3 + \cdots
\]

(10)

\[
I''_3 = \frac{1}{4} \sigma''_3(3\omega) E_0^3 + \frac{5}{16} \sigma''_3(3\omega) E_0^5 + \cdots
\]

(11)

\[
I''_5 = \frac{1}{16} \sigma''_5(5\omega) E_0^5 + \cdots
\]

(12)

As a result, we have determined the real component, \( \sigma'_n(\omega_0) \), and the imaginary component, \( \sigma''_n(\omega_0) \), of linear and non-linear complex conductivities.