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# Coordination-structural change with pressure around atmospheric pressure in Zn(II) carboxylate salts of ethylene-methacrylic acid copolymer

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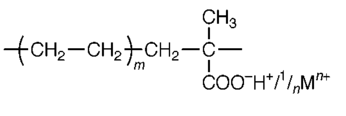
**Zn(II) carboxylate salts of ethylene-methacrylic acid copolymer undergo coordination-structural change by applying low pressure including atmospheric pressure at temperatures above 60 °C; the structure transforms from six-coordinate to four-coordinate, as the applied pressure increases from 0 to 3 MPa.**

Ethylene-methacrylic acid copolymers neutralized with metal cation (E-MAA-*x*M, see Fig. 1) are representative ionic polymers (so-called ionomers which are defined as polymers functionalized with a small amount of pendant ionic groups).[1–3] The ionic groups are frequently phase-separated from the host hydrophobic polymer matrix to form ionic aggregates, resulting in physical properties superior to the host polymer. Therefore, E-MAA-*x*M, in general, consists of three phases of amorphous polyethylene, crystalline polyethylene, and ionic aggregation regions and hence undergoes a transitional change around 60 °C ($T_i$) (loss of order inside the ionic aggregations, according to our proposal[4]) and the melting of crystalline polyethylene region near 90 °C ($T_m$). E-MAA-60Zn is one of the most popular ionomers which have been marketed as wrapping sheets for foods, and plastics for golf balls and sport shoes by Du Pont since 1964.[5] In E-MAA-*x*Zn, it is known that the Zn(II) carboxylate salts can take either four-coordination or six-coordination structures, dependent on temperature or humidity,[6–9] but we have found that the coordination structure is changed with applied low pressure between 0 and 3 MPa above 60 °C. The present letter communicates this wonderful and unique transformation of the coordination structure in E-MAA-60Zn under low pressure including atmospheric pressure.

E-MAA-60Zn was supplied from Du Pont-Mitsui Polychemicals Co. Ltd. (Tokyo), where MAA content in E-MAA is 5.4 mol% and its degree of neutralization by Zn(II) cation is 60%; E-MAA is ACR-1560 of Du Pont-Mitsui Polychemicals Co. Ltd. and E-MAA-60Zn pellets were prepared by a melt reaction of E-MAA with a stoichiometric quantity of zinc oxide in an extruder.[10] The 10–30 μm thick films for IR measurements were prepared by compression-molding the pellets at 130 °C under 19.6 MPa.

The films obtained were annealed in a vacuum oven at 130 °C for 2 h under reduced pressure with a rotary pump (around $6.7 \times 10^{-4}$ MPa because of a leak in the oven), and then cooled to room temperature at a rate of about 3 °C min$^{-1}$. After storing for more than 30 d at room temperature, this sheet was used as the starting sample in the following IR measurements. Differential scanning calorimetric measurements were made for the starting sample at a heating rate of 10 °C min$^{-1}$ by use of a Seiko Denshi SSC-5000 calorimeter. The data showed an annealing peak near 52 °C, corresponding to the transition temperature of ionic aggregates ($T_i$) and the melting peak ($T_m$) of crystalline polyethylene regions near 88 °C, being well consistent with the previous data.[4]



$$-\!\left(CH_2-CH_2\right)_m\!-CH_2-\underset{COO^-H^+/{}^1/_nM^{n+}}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-$$

**Fig. 1** Chemical structure of ethylene-methacrylic acid copolymer neutralized partially with metal cation (E-MAA-*x*M, MAA content = 5.4 mol%, M: metal cation, *x*: degree of neutralization in %).

IR spectra were measured with a Perkin-Elmer 1640 FT-IR spectrometer in the following two measuring procedures, where each trace was taken as the average of 16 scans at a resolution of 4 cm$^{-1}$.

(E-1) IR spectra under low pressures below 0.101 MPa: IR spectra were measured by use of a commercial gas cell (GL Sciences Co., Tokyo, Type GC-KBr) equipped with a hand-made heater. The starting film was placed in the gas cell two KBr windows and the pressure was controlled with $N_2$. Then, IR spectra were recorded at different temperatures.

(E-2) IR spectra under high pressures above 0.101 MPa: Under a pressure controlled by $N_2$ in an autoclave, the starting film was heated to 130 °C above $T_m$ and annealed for 2 h, and then cooled to room temperature at a rate of about 3 °C min$^{-1}$. IR spectra were recorded at 30 °C.

Fig. 2(a) shows IR spectra of the starting E-MAA-60Zn in the wave number range from 500 to 2500 cm$^{-1}$ at 30 °C. There are observed three characteristic peaks near 1624 and 1538 cm$^{-1}$, and near 1585 cm$^{-1}$, which have been assigned as antisymmetric stretching vibrations of COO$^-$, [$\nu_{as}$ (COO$^-$)], in six-(octahedral) coordination structure and that in four-(tetrahedral) coordination structure, respectively[6,7] (Coleman *et al.*[7] assumed that the 1536 and 1565 cm$^{-1}$ bands are assigned to the six-coordination structure, and the 1537 and 1620 cm$^{-1}$ bands to an acid salt structure, but here we assigned the bands at 1538 and 1624 cm$^{-1}$, and the weak band at 1565 cm$^{-1}$ which is

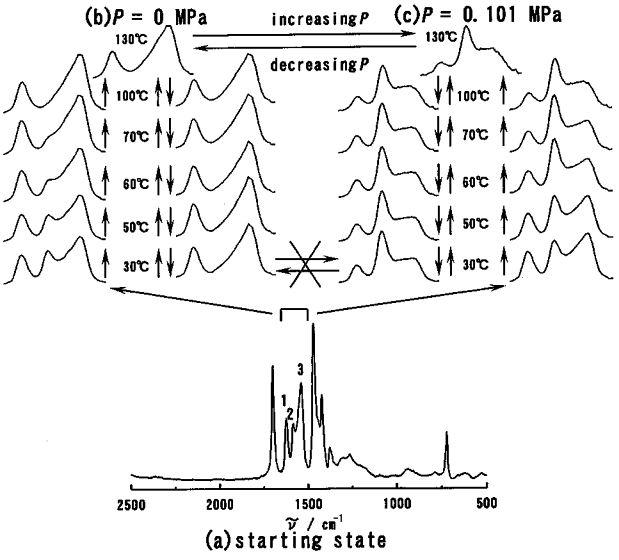


**Fig. 2** IR spectrum in the wavenumber range from 500 to 2500 cm$^{-1}$ (a), and variation of antisymmetric stretching vibration of COO$^-$ [$\nu_{as}$(COO$^-$)] with temperature under $P$ = 0 (b) and $P$ = 0.101 MPa (atmospheric pressure) (c). 1 : 1624 cm$^{-1}$, 2 : 1585 cm$^{-1}$ and 3 : 1538 cm$^{-1}$ in (a).

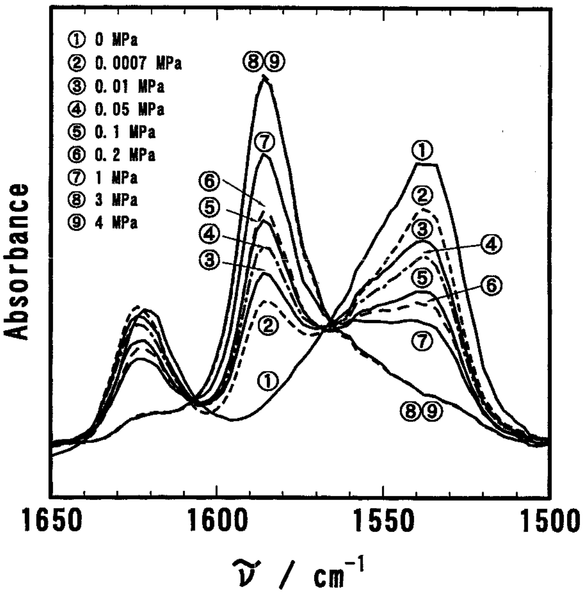


**Fig. 3** Variation of antisymmetric stretching vibrations of COO$^-$ [$\nu_{as}$(COO$^-$)] with pressure ($P$) at 30 °C. IR spectra were recorded at 30 °C for the samples cooled from the molten state of 130 °C under different constant pressures ($P$). The IR spectra (the coordination structure) are almost the same as those at 130 °C.

superimposed on the two bands, all to a six-coordination structure, because both structures are principally in six-coordination, and actually there would be a complicated distribution of the coordination structure over various structures from the six-coordination to the acid salt coordination). Fig. 2(b) and (c) show changes in the characteristic peaks of $\nu_{as}$ (COO$^-$) with varying temperature from 30 °C under two pressures [$P = 0$ (b) and $P = 0.101$ MPa (atmospheric pressure) (c) which is estimated about 0.137 MPa at 130 °C by the gaseous state function], where the measurements were done by use of the gas cell (E-1). When the starting sample is heated at $P = 0$, the $\nu_{as}$ (COO$^-$) band at 1585 cm$^{-1}$ begins to be weakened from around 60 °C and disappears at 130 °C above $T_m$ (88 °C), and as a result, only the bands at 1624 and 1538 cm$^{-1}$ are seen at 130 °C. The IR spectra at 130 °C, exhibiting the two bands at 1624 and 1538 cm$^{-1}$, are unchanged during cooling to 30 °C. On the other hand, as temperature increases under $P = 0.101$ MPa, the 1585 cm$^{-1}$ band becomes markedly intensified, accompanying the decrease of the 1624 and 1538 cm$^{-1}$ bands, and becomes predominant at 130 °C. When $P = 4$ MPa, only the band at 1585 cm$^{-1}$ was seen at 130 °C and the two bands at 1624 and 1538 cm$^{-1}$ virtually disappeared, as described later. Consequently, these IR data indicate that the Zn(II) carboxylates in E-MAA-60Zn are in six-coordination at $P = 0$ and mostly in four-coordination when $P \geq 3$ MPa. At 130 °C, as $P$ increases from 0, the coordination structure of the Zn(II) carboxylate undergoes a reversible transformation from a six-coordinate to a four-coordinate structure whose transformation rate was too fast to be detected on the present IR measurements. At 30 °C, the coordination structure, of course, is not changed with $P$, but when the temperature is elevated above 60 °C, it begins to be controlled by $P$ again.

To examine the coordination structure under higher pressure above atmospheric pressure, we made IR spectral measurements at 30 °C for E-MAA-60Zn which was cooled to room temperature, after annealing at 130 °C for 2 h under different constant pressures of $N_2$ by use of an autoclave (E-2); the results are shown in Fig. 3, where the spectrum for $P = 0$ is that in Fig. 2 which was measured by use of the gas cell (E-1). Of course, the coordination structure at 30 °C copies that at 130 °C, as already described in Fig. 2. When $P = 0$ at 130 °C, the $\nu_{as}$(COO$^-$) band appears near 1624 and 1538 cm$^{-1}$, corresponding to the six-coordinate structure, but as $P$ increases, the two bands become weaker, and the 1585 cm$^{-1}$ band is stronger, being predominant when $P \geq 3$ MPa. This pressure-dependent change was scarcely affected by the cooling rate from 130 °C. In Fig. 3, the pressure-dependent IR spectra for three $\nu_{as}$(COO$^-$) bands show two isosbestic points near 1610 and 1570 cm$^{-1}$. The existence of two isosbestic points suggests that the structural transformation results from an equilibrium change between four- and six-coordination structures.

The pressure-dependent change in the coordination structure found in this work was also observed under Ar gas and the results were almost identical to those under $N_2$. Therefore, it was concluded that the coordination structure of Zn(II) carboxylate in E-MAA-60Zn is dependent on $P$ at higher temperatures above around 60 °C. It has been reported that the coordination structure in some metal complexes is changed by adduct formation of gas molecules such as $O_2$ or under very high pressure,[10–13] but it is certainly surprising that the coordination structure changes with low pressure around atmospheric pressure. This novel finding, moreover, appears to have some significance in nature; for example it reminds us of relationships between physiological activity and coordination structure of some metal complexes in biological systems, and speaking boldly, physiological anomalies in deep sea, high mountains and cosmic space. Further studies are progressing for pressure-dependent coordination structures of metal complexes in various ionomers and also common metal complexes, for example pure metal alkyl carboxylates, in our laboratories and will be published elsewhere in the near future. In ethylene ionomers such as E-MAA-$x$M, the appearance and features of the pressure-dependent coordination structure seem to change sensitively depending on the host polymer, metal cation, its degree of neutralization and ion content.

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