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THERMAL POLYMERIZATIONS OF METAL MALEATES IN SOLID STATE

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When the thermal stabilities of a number of metal maleates in solid state were studied by means of TGA and DTA, they exhibited a remarkable exothermic process at a temperature characteristic of each metal salt. It was found that this process corresponds to the polymerization reaction of the metal maleate. In the cases of Na and Pb(II) salts, the polymer in the form of methyl esters was a brown amorphous solid (DP $\doteqdot$ 3).

It has been recognized that 1,2-disubstituted ethylene is difficult to homopolymerized. Maleic anhydride, however, has been homopolymerized by Lang and coworkers$^{1)}$, with the use of gamma-radiation and free-radical initiators. The homopolymerizations of maleic acid and its metal salt have not been reported. It is thought that a more drastic treatment might be required to carry out these difficult polymerizations. On the other hand, recently we investigated the thermal stabilities of a number of metal maleates in solid state by means of TGA and DTA, and it was observed that metal maleates could be polymerized thermally in solid state.

In this study, twelve metal maleates were prepared. Alkali and alkaline earth metal salts were prepared by neutralizations of maleic anhydride with the corresponding metal hydroxides and purified by recrystallizations from water. Other metal salts were obtained by double decompositions of sodium maleate with the corresponding metal nitrates. The precipitated metal maleates were washed repeatedly with water. All the metal maleates were dried in a desiccator and powdered below 200 mesh. The thermal behaviors of metal maleates were examined by

TG and DT methods in a nitrogen atmosphere. For the polymerizations, about 2 grams of the sample in a pyrex glass tube was heated in an electric furnace at the fixed temperature, which was determined on the basis of the data in TGA and DTA.

Fig.1 shows TGA and DTA curves of Pb(II) maleate. It can be seen in this figure that there is an exothermic process at 270°C. In the cases of other metal salts, such an exothermic process also occurred at a temperature characteristic of each metal salt. Only with the heavy metal salts, some loss in weight was accompanied by this process, and at the same time maleic anhydride was partly liberated. Since the formation of the anhydride from the metal maleate may be endothermic rather than exothermic, it is suggested that this process is not concerned with the formation of the anhydride.

During the exothermic process in Pb(II) maleate, the specimen was expanded momentarily and became light brown colored. The resulting product was proved to be an amorphous solid by X-ray diffraction measurement. It was also confirmed by IR spectroscopy that the product is a saturated metal carboxylate. The similar results were obtained with sodium maleate. Accordingly, it seems that the exothermic processes can be regarded as the polymerization reactions of these metal

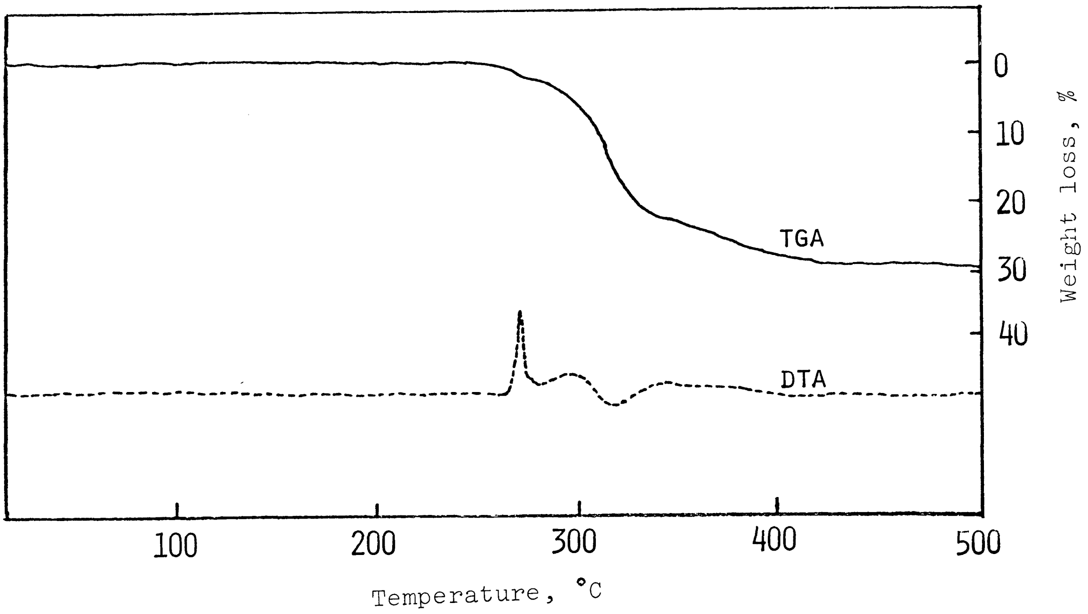

Fig.1. TGA and DTA curves of Pb(II) maleate.

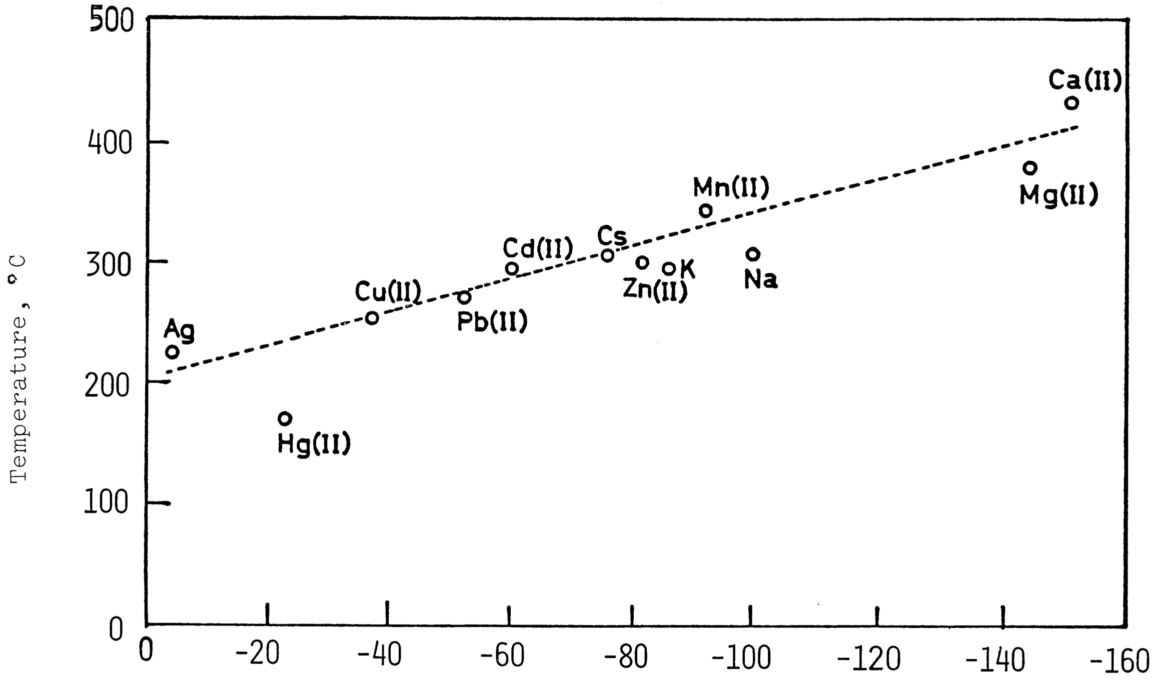

Fig.2. Correlation of exothermic temperatures with the standard heats of formation of metal oxides$^{2)}$.

maleates. The heats evolved through this process may correspond to the so-called heats of polymerization.

The exothermic processes in other metal maleates may be also regarded as the polymerization reactions, though the polymerized products themselves could not be isolated in these cases because of the succeeding thermal decompositions. The temperatures at which the exothermic processes occurred, increased with the heats of formation of the corresponding metal oxides (Fig.2). The heats of formation of metal oxides may be an approximate measure of the bond energies between metal ions and oxygen ions in the metal formates$^{3)}$. This may be also the case for the metal maleates. On the other hand, as for the formation of the polymer in the solid crystalline matrix, it seems to be necessary that the initial monomeric units in the crystal are rearranged geometrically favorable for the polymerization$^{4)}$. Such a rearrangement may be facilitated as the strength of the metal-oxygen bond becomes weaker. Thus it can be understood that the polymerization temperatures increase with the heats of formation of metal oxides.

Sodium polymaleate was obtained at 300°C in the electric furnace. Lead(II) maleate could be also polymerized between 250°C and 265°C by the same method. In these polymerizations the temperature controll is particularly important since the local overheating due to the heats evolved is liable to cause the succeeding thermal decomposition, accompanied by the evolution of gases (mainly CO_2). For these salts, however, it is possible to distinguish clearly between the polymerization reaction and the thermal decomposition under the sufficient temperature controll.

Sodium polymaleate and the corresponding acid are very soluble in water and make brown colored solutions, respectively. Lead(II) polymaleate is insoluble in water, but its acid is also very soluble in water. Found : C,41.43; H,3.39%. Cald for $(C_4H_4O_4)_n$: C,41.39; H,3.47%. NMR (DMSO-d_6) : τ near 7.6 (1H, methine), 0∿1 (1H, carboxyl). Either methyl ester from the silver salt and methyl iodide is a red-brown amorphous solid (mp 115∿120°C). The molecular weight of the precipitated each methyl ester was determined by the freezing point depression with a solvent of dimethyl sulfoxide, giving a same value of about 420, or a $\overline{DP}$ of about 3. These results may indicate that the polymer has a six ring structure. It seems likely that, at the considerably high temperatures mentioned above, high polymers are not formed. The characteristics of this polymer, however, are somewhat different from those of hexahydromellitic acid$^{5)}$.

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