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Thickening of polyester resins with MgO: Structural study of a model magnesium carboxylate

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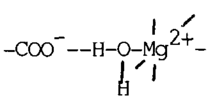
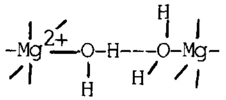
Summary

The crystal structure of magnesium 1-methylethylene bis-o-phtalate heptahydrate, a a model for thickened polyester resins, was determined by X-ray analysis. This compound presents a layered structure with alternating polar and non-polar areas. Water molecules are involved in crystal formation through  $-COO^{-}--H-O-Mg^{2+}-$ and  $-Mg^{2+}-O-H---O-Mg-$ hydrogen bonds showing that water might play a cohesive role in the ionic aggregates of thickened polyester resins.

Introduction

The reaction of metal oxides such as magnesium or calcium oxide with polyester resins containing carboxyl end groups leads to compounds with very high viscosities and is referred to as the thickening reaction of polyester resins.

This increase in viscosity has been extensively studied by several authors. Different mechanims were proposed :

Starting from the formation of basic or neutral magnesium carboxylates, Vancso-Szmercsayi's mechanism (1-6) involves coordinate bonding between ester groups and magnesium ions, leading to a network structure.

According to Burns and Gandhi (7-8) the formation of linear ionic macromolecules by coupling of magnesium carboxylate chain ends could account for the observed increase in viscosity.

In a previous study (10-11) on low molecular weight models and on well defined difunctional oligomers, we showed that these two mechanisms could not fit some of our experimental results. A better approach of the mechanism of this reaction was found in the formation of ionic aggregates of magnesium carboxylates, followed by the entanglement of attached polyester chains leading to high viscosity compounds, as in ionomers.

A recent and interesting study by Balakoteswara and Gandhi (12) on industrial-like polyester resins fits our previous conclusions :

According to these authors, the presence of both basic and neutral magnesium salts in thickened polyester resins, and the shape of viscosity-time curves do not fit the polymerization or the coordinate complex mechanisms, but fit better a mechanism involving the formation of ionomer-like aggregates. Moreover small-angle X-ray scattering studies showed the

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presence of the so-called "ionomer peak" at $2\theta \simeq 3°$. Although this SAXS study was carried out on a medium rather different from the usual ones - dried residue of the centrifugated acetone solution of a thickened polyester - this result is important. The transmission electron microscopy study of these authors is less convincing due to the lack of information on the 50-60 Å domains of the observed granular structures.

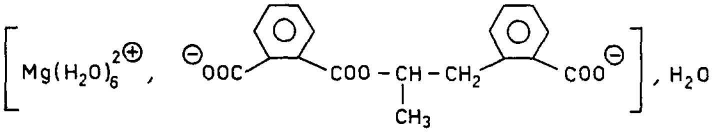
The role of water on thickening kinetics and on the value of plateau viscosity at high reaction thickening times has long been known (2-9) : the presence of water leads to an increase of thickening rate in the earlier stages of the reaction and to a decrease of the value of plateau viscosity in the last stages of the reaction.

However the role of water is only poorly understood at present, and moreover the chemical structure of magnesium carboxylate aggregates can only be postulated.

To get more light on the aggregate structure, and on the bonding of solvation water on magnesium carboxylates, the crystal structure of a low molecular weight model, magnesium-1-methylethylene-bis-o-phtalate was investigated by X-ray analysis.

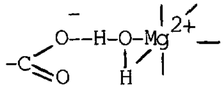
Results and discussion

A monocrystal of magnesium-1-methylethylene-bis-o-phtalate was obtained by recrystallization in water. It crystallizes with 7 molecules of water, 6 of them coordinated to the central magnesium ion. The chemical formula of the salt is therefore :



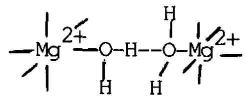
Its crystal structure investigated by X-ray analysis (13) is illustrated in Fig. 1.
Several remarks can be made :

-There are no real magnesium carboxylate groups, since carboxyls are H-bonded to the coordination water of the central magnesium ion :



- A true network of H-bonds appears and favors the cohesion of the crystal (Fig. 2). Three kinds of H-bonds can be detected :

H bonds between atoms within repeating unit,
H bonds between atoms of upper or lower repeating units,
H bonds between magnesium ions of lateral repeating units:



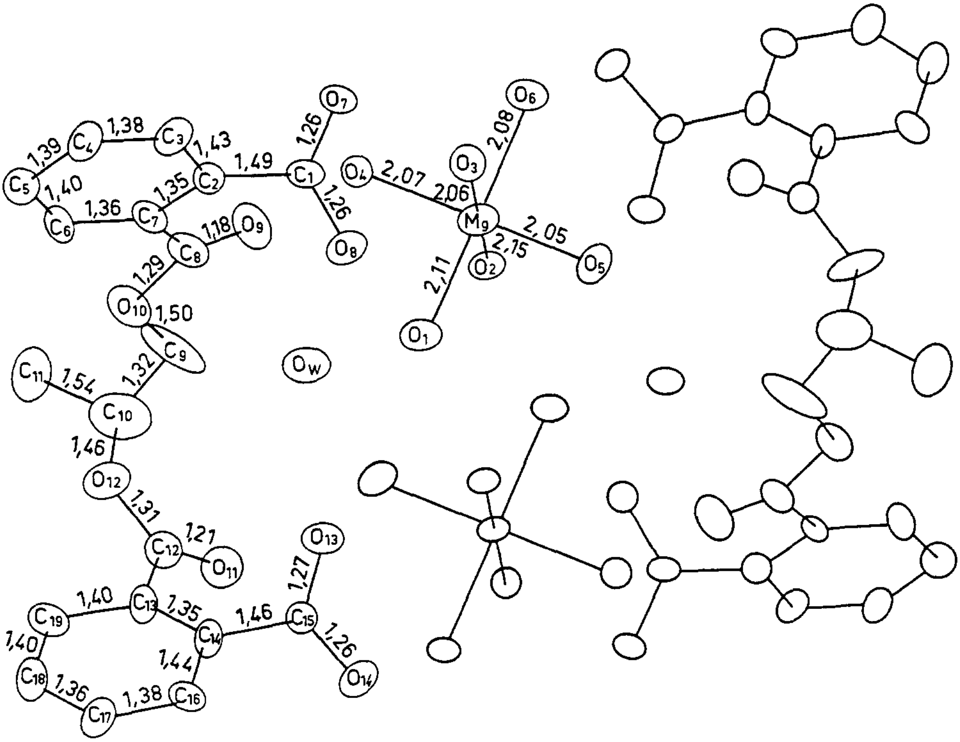


Figure 1 : Crystal structure of magnesium-1-methylethylene-bis-o-phthalate heptahydrate (centrosymetric spacial group $P_{\bar{1}}$).

Triclinic system: a = 6.93 Å α = 97.63^d

b = 11.13 Å β = 93.08^d

c = 16.81 Å γ = 105.76^d

Interatomic distances (Å) are given on the figure.

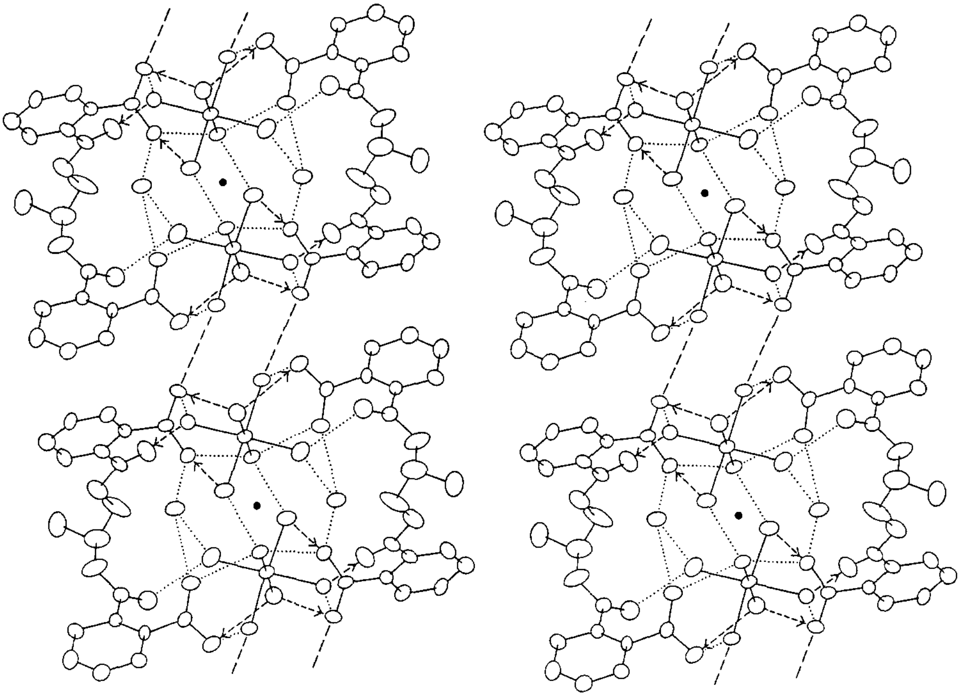


Figure 2 : Crystal structure of magnesium-1-methylethylene-bis-o-phthalate heptahydrate : H-bond network.

.... : H-bonding within repeating unit

------- : H-bonding between lateral repeating units

------➤ : H-bonding between upper or lower repeating units.

The crystal, then is made up of polar layers of $Mg(H_2O)_6^{2+}$ and carboxylate groups, separated by non-polar layers of phenyl and 1-methylethylene groups.

In thickened polyester resins, water content is much lower (~1 mol H_2O / mol COOH), polyester chains are polydispersed and neutralization is usually not complete. Such a regular arrangement is thus unlikely. However, the crystal structure determined here is not incompatible with the existence, in thickened polyester resins, of ionic aggregates in which extensive H-bonding between water and basic magnesium carboxylates, neutral magnesium carboxylates or unreacted magnesium oxide could take place. Water might not play a role only of plastification of ionic domains as assumed by Balakoteswara and Gandhi (12), but also a role in the cohesion of these domains. The relation between plateau viscosity and water content might not be as simple as that ($\mathrm{Log}_{10} \propto 1/_{H_2O}$) proposed by these authors.

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