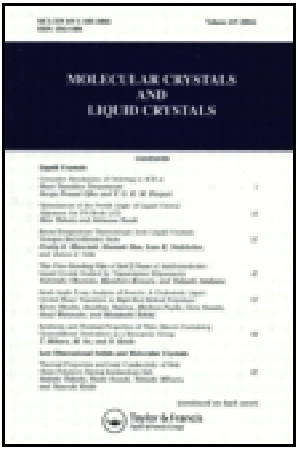

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Poly(Carboxylic Acids)-Metal Salts Complexes: Formation, Structure, and Application in Dentistry

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POLY(CARBOXYLIC ACIDS)-METAL SALTS COMPLEXES: FORMATION, STRUCTURE, AND APPLICATION IN DENTISTRY

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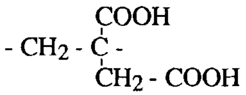
Abstract It has previously been shown that poly(carboxylic acids) such as poly-(acrylic acid) can form hydrogels with $FeCl_3$, $TiCl_3$, $ZrCl_4$, and $HfCl_4$ which may be used for the tightening of channels in hard tissues of human teeth (dentin) and decrease their permeability for fluids and ions. This paper presents results on the formation of metal (Ti(IV), Zr(IV), Hf(IV)) salt complexes with two other poly-(carboxylic acids) such as poly(itaconic acid) and poly(maleic acid). Salts formed are brittle, nonsoluble glasses and do not form hydrogels. For that reason they can not be used for tightening of channels in e.g. human dentin.
FTIR spectroscopy and SEM microscopy were used for studying the structure and morphology of these salts.

INTRODUCTION

Human teeth contain micro-diameter channels. In enamel, dentin, and root cementum these channels are filled with a natural biohydrogel, which plays an important role in transportation of ions and molecules [1]. In dentin, the channels (tubules)(Fig.1) are also pathways for bacteria during tooth decay (caries). In order to prevent caries progression it is important to block penetration of bacteria but not limit transportation of ions in the dentin. For this reason we have developed a technique to increase the density of the natural gel by blocking the channels with polymeric, water-swollen hydrogels.
We have studied hydrogels of poly(acrylic acid) poly(propenoic acid) with Fe(III) [2] and Ti(IV), Zr(IV), Hf(IV) [3] salts, which can efficiently tighten channels in dentin (Fig.2). In order to test other water soluble poly(carboxylic acids) we have chosen poly(itaconic acid)(poly(methylenesuccinic acid)) and poly(maleic acid)(poly(2-butanedioic acid)) and studied the formation of their salts with $TiCl_4$, $ZrCl_4$ and $HfCl_4$. The results of this research is presented in this paper.

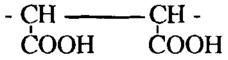
EXPERIMENTAL SECTION

Poly(itaconic acid)(poly(methylenesuccinic acid))(PIA) and poly(maleic acid)(poly(2-butanedioic acid))(PMALA) were delivered by Polyscience (USA). $TiCL_4$(liquid) and $ZrCl_4$, $HfCl_4$ (solids) were delivered by Aldrich (Germany). For the preparation of salts, 2 % (wt) water solution of PIA (or PMALA) and 10% (wt) water solution of $MeCl_4$ ($TiCl_4$, $ZrCl_4$ and $HfCl_4$) were mixed together at different molar ratios.



$$-CH_2-\underset{CH_2-COOH}{\overset{COOH}{C}}-$$

(PIA)



$$-\underset{COOH}{CH}-\underset{COOH}{CH}-$$

(PMALA)

UV/VIS spectroscopy (Beckman 7500) does not show any significant changes in the spectra of salts and their components that could be used for the interpretation of their structures. FTIR spectroscopy (FTIR Perkin Elmer 1650) was made using KBr pellets. DSC scan measurements were made on powdered samples (3.0 ± 0.1 mg) in covered aluminium pans using a Perkin-Elmer DCS4 thermal analysis system. SEM microphotographs were made with a Jeol JSM-820 scanning microscope.

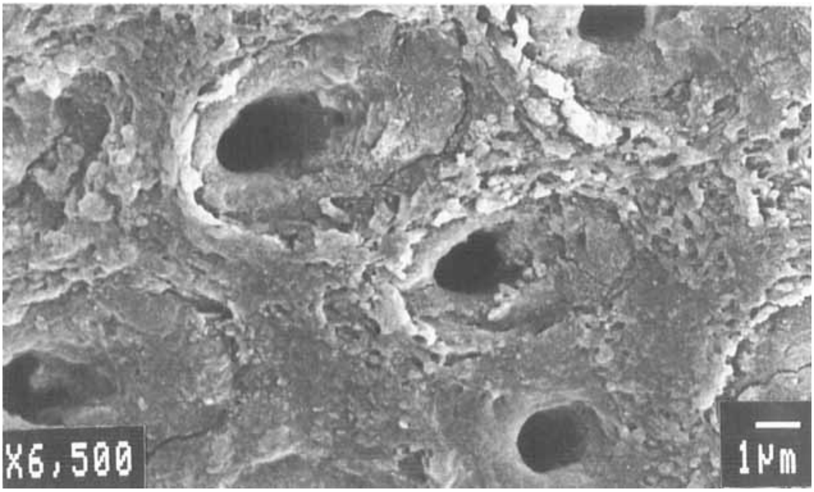


FIGURE 1 SEM microphotograph of channels (tubules) in human dentin.

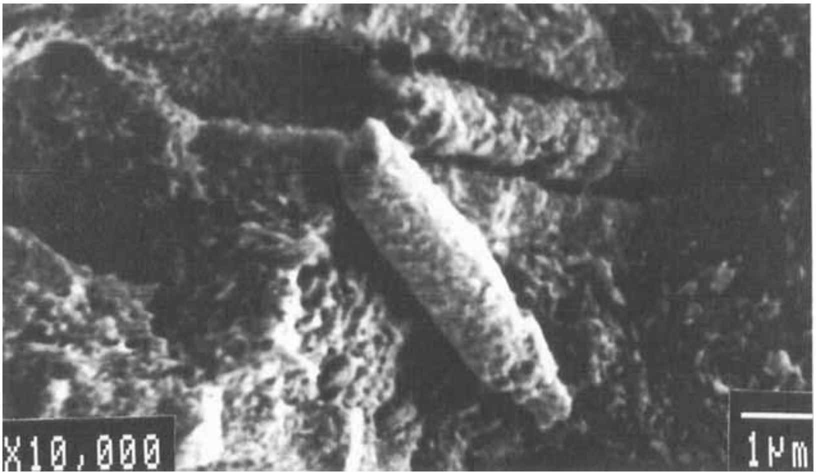


FIGURE 2 SEM microphotograph of tubule blocked by poly(acrylic acid)--Zr(IV) hydrogel.

RESULTS AND DISCUSSION

It is well known that $TiCl_4$, $ZrCl_4$, and $HfCl_4$ (Group IVA salts) give different hydrolysis products when dissolved in water (exotermic reactions). However, the hydrolysis mechanism is the same and occurs in the following steps: [4-7]

$$MeCl_4 + H_2O \longrightarrow MeCl_3OH + HCl \qquad (1)$$
$$MeCl_3OH + H_2O \longleftrightarrow MeCl_2(OH)_2 + HCl \qquad (2)$$
$$MeCl_2(OH)_2 + H_2O \longleftrightarrow MeCl(OH)_3 + HCl \qquad (3)$$
$$MeCl(OH)_3 + H_2O \longleftrightarrow Me(OH)_4 + HCl \qquad (4)$$

where Me = Ti, Zr, or Hf.

At pH=1 (HCl formed from hydrolysis) Zr and Hf salts exist in water solution as $MeCl_2(OH)_2$ and can be crystalized as $MeCl_2(OH)_2\ 7H_2O$ giving needle-like crystals (Fig.3 and Fig.4).

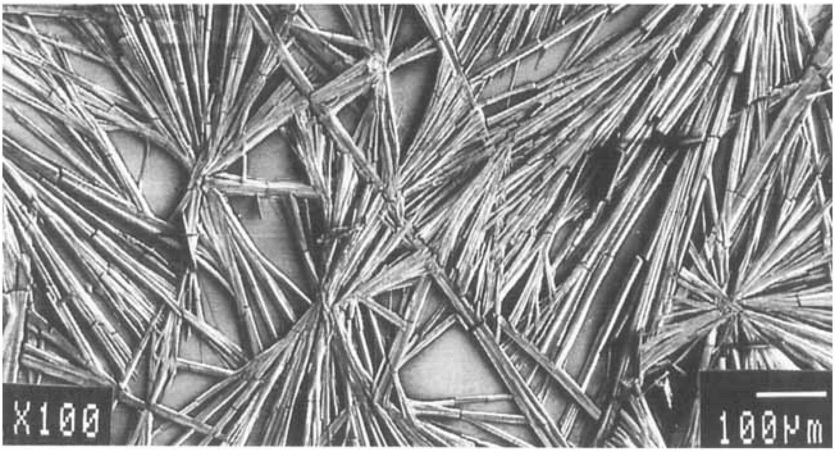


FIGURE 3 SEM microphotograph of $ZrCl_2(OH)_2\ 7H_2O$ crystals.

FIGURE 4 SEM microphotograph of $HfCl_2(OH)_2\ 7H_2O$ crystals

The first stage of the hydrolysis of $TiCl_4$ is titanium hydroxytrichloride $Ti(OH)Cl_3$, a yellow spongy compound, which in the second stage is further hydrolyzed to titanium dihydroxydichloride $Ti(OH)_2Cl_2$, a yellow solid. The third stage of hydrolysis is represented by titanium trihydroxychloride $Ti(OH)_3Cl_2$ H_2O, which is formed as a white powder. (Fig.5). [8-11]

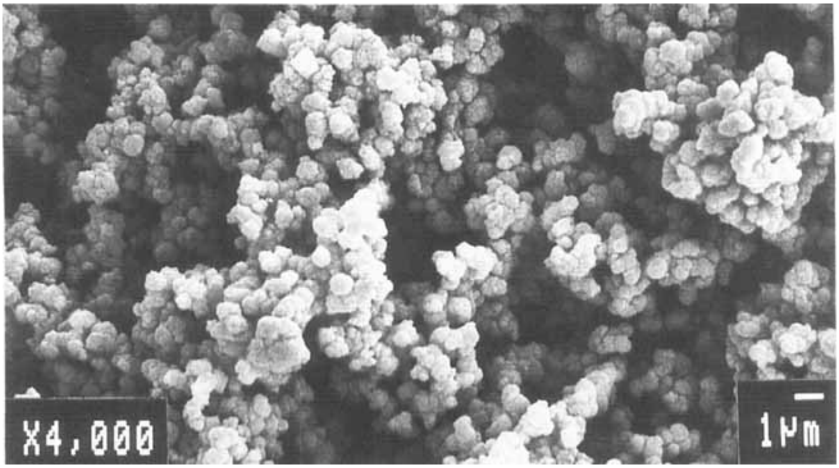


FIGURE 5 SEM microphotograph of $Ti(OH)_3Cl$ $2H_2O$ powder.

IR spectra of these hydrolysed salts (Fig.6) show that all contain absorbtion bands at 1627 and 3500-3000 cm^{-1} that is characteristic for the presence of water (OH groups). The detailed interpretation of these IR spectra as a function of water content has been given elsewhere.[5]

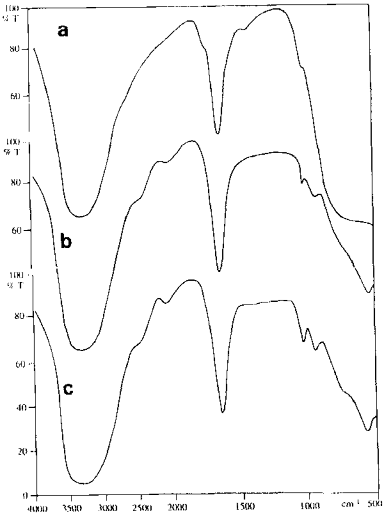


FIGURE 6 FTIR spectra of: (a) $Ti(OH)_4$ (TiO_2 $2H_2O$), (b) $ZrCl_2(OH)_2$ $7H_2O$ and (c) $HfCl_2(OH)_2$ $7H_2O$

Reactions of $ZrCl_4$ with aliphatic acids in water-free conditions at -15°C give mainly addition compounds of the type $ZrCl_4$ 2RCOOH. However, after heating to room temperature (21°C) hydrogen chloride is eliminated and products are obtained that appear to have composition stuctures represented by $ZrCl_2(RCOO)_2$ 2RCOOH.[12]

All these zirkonium compounds have very low stability against hydrolysis and therefore difficulties are encountered in isolating and characterizing pure products.

For dental applications of Group IVA salts, all reactions have to proceed in the presence of water, which is a permanent component (saliva) in the human oral cavity.

Salts of PIA and PMALA with Group IVA salts were obtained in water solution. After mixing PIA (or PMALA) solutions with solutions of $MeCl_4$, the hydrogels do not precipitate. After drying, the remaining materials are brittle solids (Fig.7 and Fig.8) (with similar macro-structures for all salts).

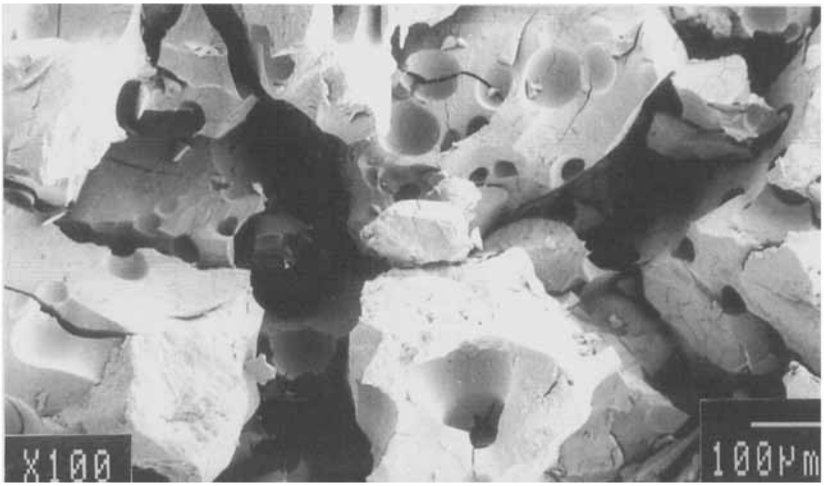


FIGURE 7 SEM microphotograph of PIA-Zr(IV) salt

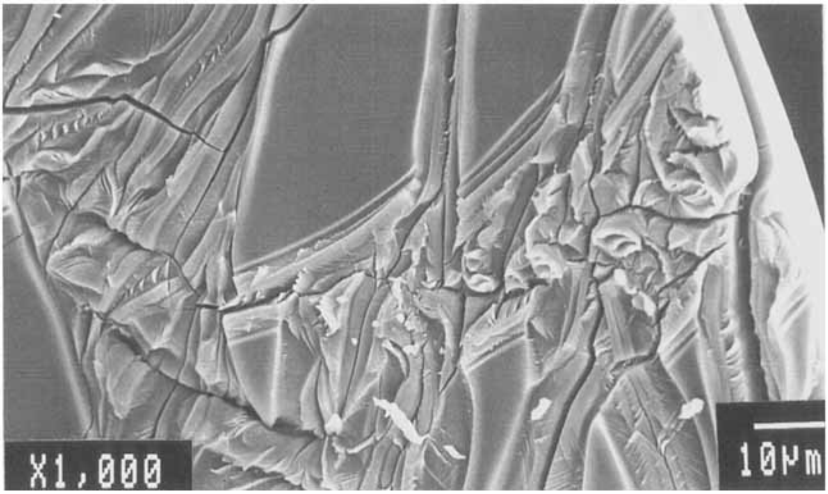


FIGURE 8 SEM microphotograph of PMALA-Ti(IV) salt

However, all PIA-Ti(IV), Zr(IV) or Hf(IV) solids have a granular micro-structure (Figs.9-11), whereas PMALA-Ti(IV), Zr(IV) and Hf(IV) solids are glassy materials with different morphology (Figs.12-14.)

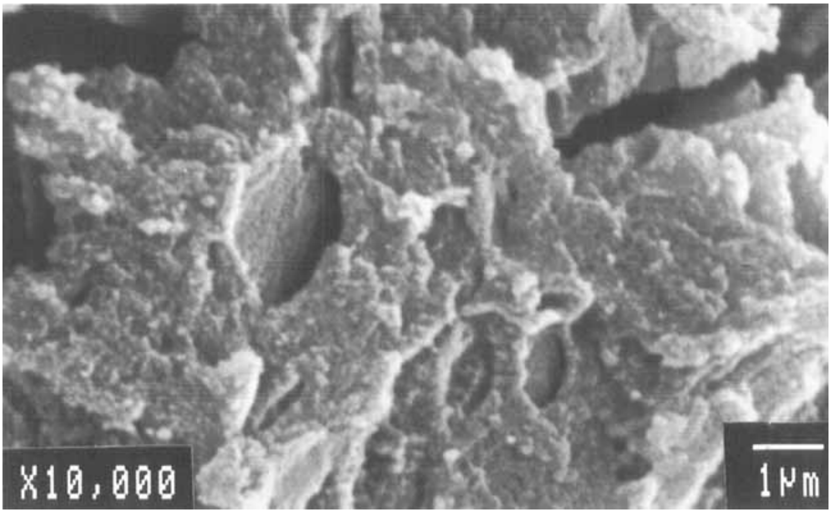


FIGURE 9 SEM microphotograph of the solid PIA-Ti(IV) salt

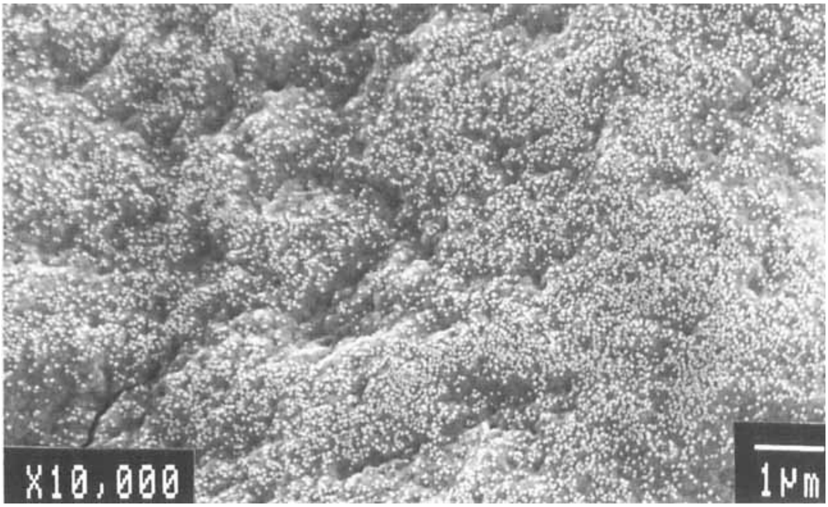


FIGURE 10 SEM microphotograph of the solid PIA-Zr(IV) salt

FIGURE 11 SEM microphotograph of the solid PIA-Hf(IV) salt

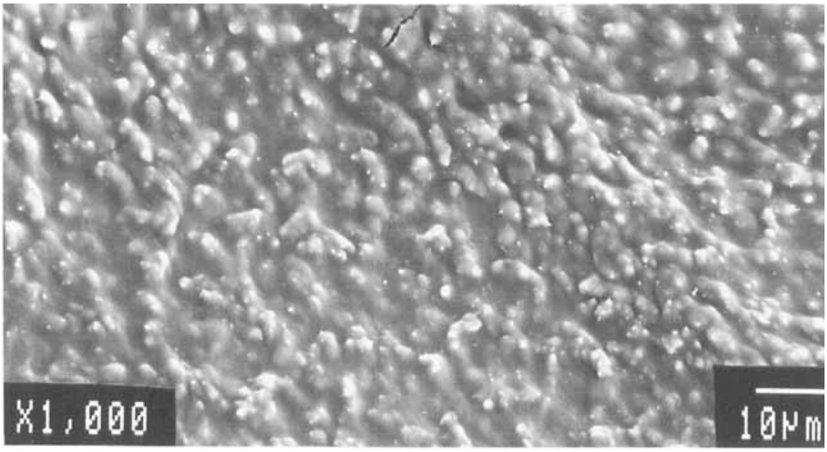


FIGURE 12 SEM microphotograph of the glassy PMALA-Ti(IV) salt

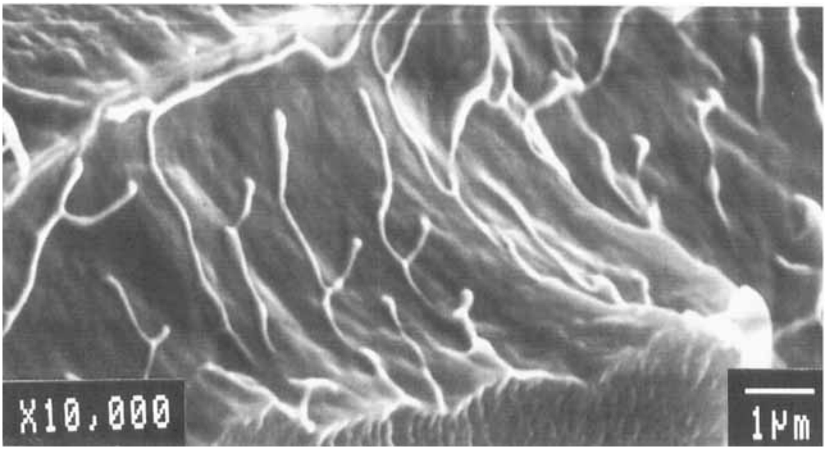


FIGURE 13 SEM microphotograph of the glassy PMALA-Zr(IV) salt

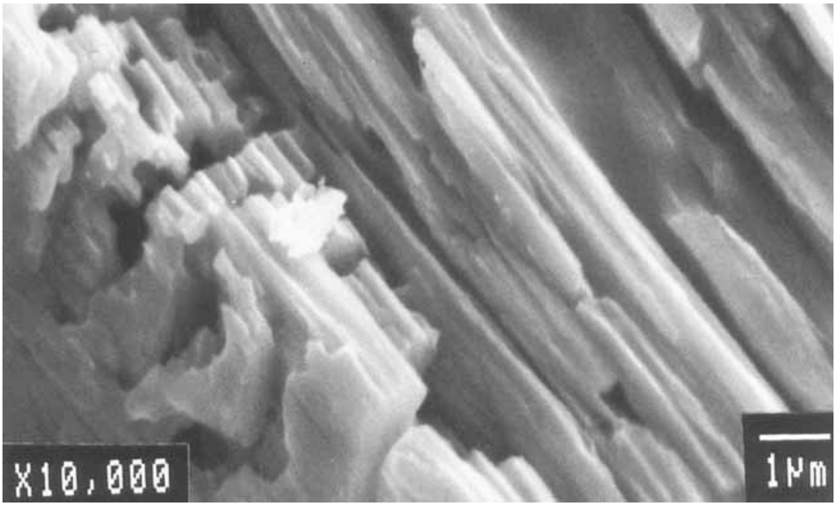


FIGURE 14 SEM microphotograph of the glassy PMALA-Hf(IV) salt

DSC measurements do not show presence of any glass transition temperature (T_g) or melting temperature (T_m) in the examined samples. After heating they lose their coordination water, and take on different colors.:

Yellow: PIA-Ti(IV) (at 160°C), PIA-Zr(IV) (155°C), PIA-Hf(IV) (180°C), PMALA-Ti(IV) (170°C), PMALA-Zr(IV) (140°C), and PMALA-Hf(IV) (200°C).

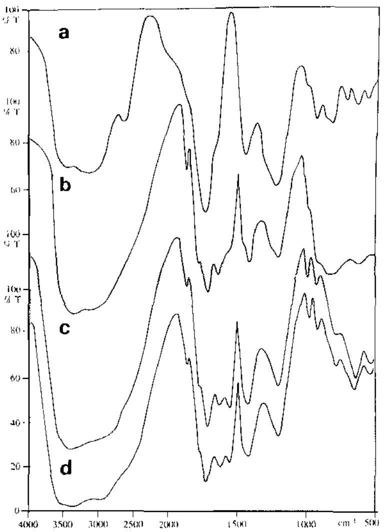
Brown: PIA-Ti(IV) (at 200°C), PIA-Zr(IV) (200°C) , PIA-Hf(IV) (250°C), PMALA-Ti(IV) (230°C), PMALA-Zr(IV) (280°C), and PMALA-Hf(IV) (240°C).

Black: PIA-Ti(IV) (240°C), PIA-Zr(IV) (285°C), PIA-Hf(IV) (300°C), PMALA-Ti(IV) (280°C), PMALA-Zr(IV) (340°C), and PMALA-Hf(IV) (360°C).

The products of PIA or PMALA reactions with Group IVA salts are believed to be crosslinked as evidenced by the product's lack of solubility in water, organic solvents, and in concentrated HCl (except PIA-Ti(IV) and PMALA-Ti(IV)). This is a crude but often used measure of crosslinking.

FTIR spectra of pure PIA, PMALA and their salts with $TiCl_4$, $ZrCl_4$, and $HfCl_4$ are shown in Fig.15 and Fig.16, respectively. Comparisons of these spectra indicate large similarites, since PIA salts with different metal ions Ti(IV), Zr(IV) and Hf(IV) (Fig.15) have almost identical structures. The same conclusion can be made for PMALA salts with Ti(IV), Zr(IV) and Hf(IV) (Fig,16.).

The abnormally strong hydrogen bridges between the carbonyl and hydroxyl groups of two carboxylic acid groups in the PIA and PMALA make the O-H stretching vibrations so distorted from the normal , that they give a very broad band at 3500-3000 cm^{-1} (Fig 15a and 16a). The main peak of the OH absorbtion in PIA and PMALA is at 3174 cm^{-1} and 3029 cm^{-1} respectively, followed by a main satelite band at 2614 cm^{-1} (PIA) and 2662 cm^{-1} (PMALA) (Fig.15a and Fig.16a).



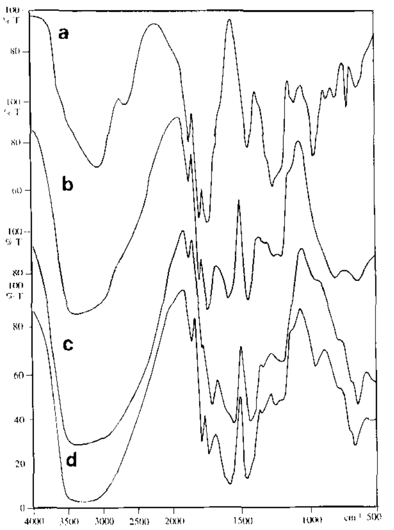


FIGURE 15 FTIR spectra of: (a) pure PIA, (b) PIA-Ti(IV); (c) PIA-Zr(IV); (d) PIA-Hf(IV) salts obtained at molar ratio of PIA:$MeCl_4$ (2:1)

FIGURE 16 FTIR spectra of: (a) pure PMALA; (b) PMALA-Ti(IV); (c) PMALA-Zr(IV); (d) PMALA-Hf(IV) salts obtained at molar ratio of PMALA:$MeCl_4$ (2:1)

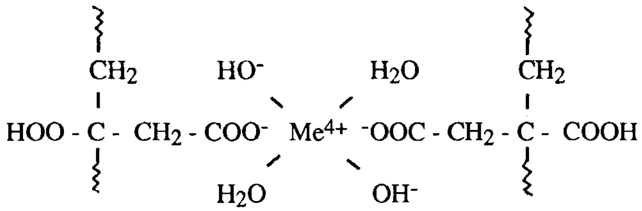
The absorbtion between 2700-2500 cm^{-1} is also a strong evidence for the presence of strongly bonded OH groups. Although bonds of this strength are unusual in polymers other than poly(carboxylic acids). PIA and PMALA show strong bands at 1728 cm^{-1} and 1712 cm^{-1} respectively, associeted with the C=O anti-symmetrical and weaker band at 1418 cm^{-1} with the symmetrical stretching vibrations. At 1196 cm^{-1} (PIA and 1237 cm^{-1} (PMALA) is a band that results from the coupled C-O and OH in-plane deformation modes. In poly(acrylic acid) this band lies at 1240 cm^{-1} and is strongly characteristic for the presence of syndiotactic structures. In the isotactic form, it splits into two bands at 1215 and 1275 cm^{-1}.

FTIR spectra of PIA-Ti(IV), ZR(IV), Hf(IV) (Fig.15b,c,d), and PMALA-Ti(IV), Zr(IV), Hf(IV) (Fig.16b,c,d) salts show that carboxylic bands at 1728 cm^{-1} (PIA) and 1712 cm^{-1} (PMALA) disappear in reaction with $MeCl_4$ salts, and a new band characteristic for the formation of ionized carboxyl groups at 1560-1570 cm^{-1} appears. This band is characteristic for the anti-symmetrical vibrations of the ionized carbonyl group (COO^-), and is accompanied by the band increasing at 1420 cm^{-1} which belongs to the symmetrical vibration of the ionized carboxyl group (COO^-). At the same time, a broad band with maximum around 3450 cm^{-1} increases, which is probably due to the presence of water ligands in the examined salts. In addition, all salts show the presence of a band around 1720 cm^{-1}, which belong to the unreacted carboxylic groups.

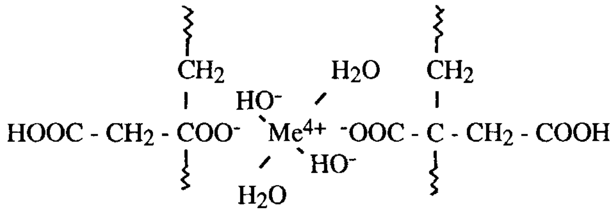
It can be estimated that no more than 60-70% of all carboxylic groups present in PIA or PMALA react with $MeCl_4$ salts. The most probable mechanism of the formation of PIA-Me(IV) and PMALA-Me(IV) salts (which is the same for PIA and PMALA) can be described as follows:

$$MeCl_2(OH)_2 + 2\ \text{-COOH} \longrightarrow \text{-COO}^-Me(OH)_2^{2+}\ {}^-\text{OOC-} + 2\ HCl$$

The most common coordination number of metals of Group IVA is six (recognised for all oxidation states of the metals), although compounds are known in which the coordination number is 4, 5, 7, or 8. For the coordination number six in aqueous environments, the six ligands have to be attached to metal cations: two COO^-, two OH^-, and two H_2O. The possible inter-molecular structures in PIA and PMALA salts are shown below:



(5)



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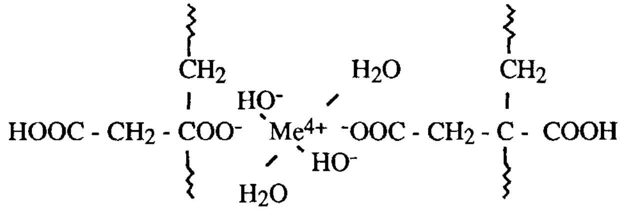
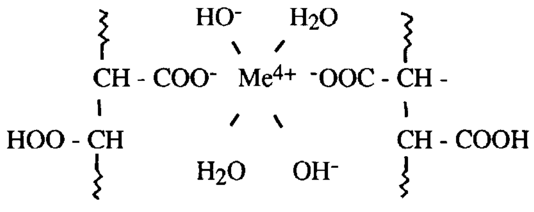


(7)

PIA-Me(IV) salts



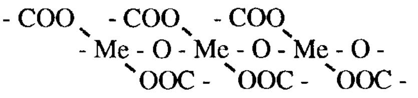
(8)

PMALA-Me(IV) salts

The formation of inter-molecular PIA-Me(IV) and PMALA-Me(IV) salts causes an ionic-type of crosslinking of poly(carboxylic acids) molecules. However, the formation of of intra-molecular salts is also possible.

When the aqueous solutions of these salts are dried at 60-120^{0}C all coordination water is removed, and from the two hydroxyl groups -O-Me-O-Me-O- type chains (bands in the range 840-970 cm^{-1}) are formed (Fig.15 and 16). The band in the region 560-580 cm^{-1} is apparently due to the vibrations of the Me-O-Me single bond.

The dried salts are completely insoluble, because of lack of OH^{-} groups, and they have probably the following structures:



$$\begin{array}{l} \mathrm{-COO}\diagdown\ \ \mathrm{-COO}\diagdown\ \ \mathrm{-COO}\diagdown \\ \qquad \mathrm{-Me-O-Me-O-Me-O-} \\ \qquad \diagdown\mathrm{OOC-}\ \ \diagdown\mathrm{OOC-}\ \ \diagdown\mathrm{OOC-} \end{array}$$

Since the substitution of carboxylic groups in PIA and PMALA is not 100% (maximum 60-70%, determined from the substraction of FTIR spectra, for different molar ratios PIA or PMALA:MeCl$_4$ = 10:1, 2:1, 1:1, and 1:2, 1:10), the elementary analysis (H, C, O, Me in %) does not allow determination of structure of these salts.

CONCLUSIONS

Poly(itaconic acid) (PIA) and Poly(maleic acid) (PMALA) give unsoluble, strongly crosslinked salts with TiCl$_4$, ZrCl$_4$, and HfCl$_4$,salts in water solution. Because both PIA and PMALA do not form hydrogels like poly(acrylic acid) with MeCl$_4$ salts,[4] they can not be used for the tightening of micro-channels in teeth.

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