

Structure of Poly(acrylic acid)–Hf,Ti,Zr(IV) Chloride Gels and Their Potential Application in Dentistry

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SYNOPSIS

Poly(acrylic acid) [poly(propenoic acid)] (PAA) can form stable and insoluble, colorless hydrogels with HfCl₄, TiCl₄, and ZrCl₄ in water. Two carboxylic groups of PAA are complexed by the M(OH)₂²⁺ ions. Hydrogels formed from PAA–MCl₂(OH)₂ (where M = Hf, Zr) (2 : 1) have found practical application in the blocking of microscopic channels in tooth dentin, and thereby decrease the fluid permeability and protect against tooth decay. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(acrylic acid) [poly(propenoic acid)] (PAA) forms gels on the addition of inorganic metal salts. The PAA–iron(III) chloride gel has been found to be useful for the plugging of tooth microchannels (tubules),¹ and its structure was investigated in detail.^{1–3} The great disadvantage of PAA–iron(III) chloride gel is its yellow-brown color, which limits its application in dentistry because of aesthetic reasons.

The most common coordination number of hafnium (Hf), zirconium (Zr), and titanium (Ti) (metals IV group) is six (recognized for all oxidation states of the metal), although compounds are known in which coordination number is 4, 5, 7, or 8.⁴ The majority of complexes formed by M(IV) chlorides are six-coordinate complexes of the type M(metal)Cl₄ · 2L or MCl₄ · B (where L = unidentate ligand and B = bidentate ligand).

The reaction of metal(IV) chlorides with aliphatic acids has been studied by several investigators,^{5–9} and there is much disagreement among the various investigators regarding the structures of reaction products. Among the many reported reaction products are mono-, di-, tri-, and tetrasubstituted compounds as well as various compounds containing co-

ordinated aliphatic acid and hydrogen chloride. Some of the contradictory observations reported in the literature are undoubtedly due to the recognized complexity of chemical behavior of metals group IV.^{10–12} Many compounds of this group have very little stability toward hydrolysis, and therefore, experimental difficulties are encountered in isolation and characterization of pure reaction products.

The reason for this work was to study the structure and dental application of poly(acrylic acid)–Hf,Ti,Zr(IV) chloride gels which are colorless. Plugging of microdiameter channels (tubules) in the enamel and dentin of human teeth is one of possible way of limiting the penetration of bacteria during teeth decay (caries) and has a great practical importance.

EXPERIMENTAL

Poly(acrylic acid) (PAA) (Aldrich, molecular weight 5000, with an average of 70 carboxylic groups per molecule). Metal Hf, Ti, and Zr(IV) chlorides (Merck) (M(IV) were used without purification.

For PAA–M(IV) hydrogen preparation a 5 wt % of PAA and 5 wt % of M(IV) chlorides in water were prepared separately. After a mixing of these solutions in a required PAA : M(IV) molar ratio (e.g., 2 : 1), the white insoluble hydrogel is immediately precipitated. Dissolution of M(IV) chlorides in water is a rapid exothermic reaction.

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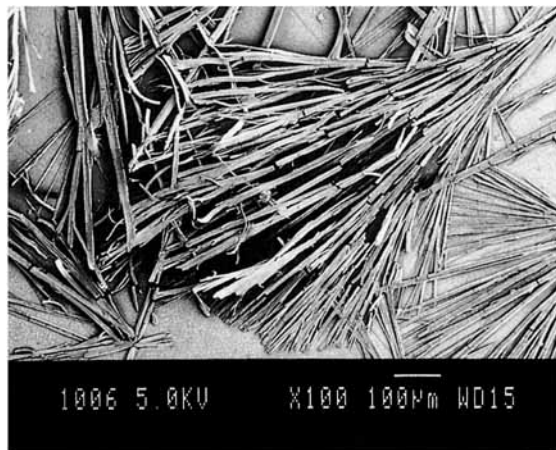


Figure 1 SEM photomicrograph of $\text{HfCl}_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ crystals.

Partially hydrolyzed M(IV) chloride salts as $\text{HfCl}_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, $\text{ZrCl}_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ti}(\text{OH})_4(\text{TiO}_2 \cdot 2\text{H}_2\text{O})$ were obtained by evaporation of water at room temperature.

UV-vis and IR spectra were recorded with Beckman 7500 UV-vis and FT-IR Perkin Elmer 1650 spectrometers, respectively. UV-vis spectra of thin layers of swollen PAA-M(IV) hydrogels were made on the surface of a quartz cuvette, whereas IR spectra were measured from the dried (at room temperature) hydrogels dispersed in KBr pellets.

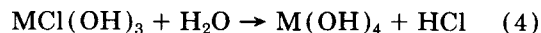
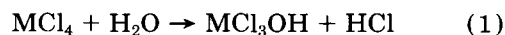
Thermal analysis was performed with a Pauli Derivatograph; 7-mg samples were run in air over the temperature range 25–500°C. Al_2O_3 was used as a standard.

SEM photomicrographs were made with the Jeol JSM-820 scanning microscope. Water from microgels for SEM was removed by the liophilization process, which allows “freezing” of the original structure of a swollen gel.

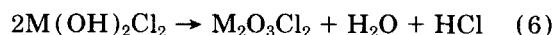
The transportation of water through channels in teeth was measured with a device constructed by Lindén and Källskog in our institute; details on this equipment were published elsewhere.¹

RESULTS AND DISCUSSION

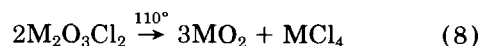
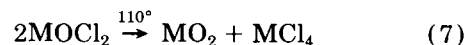
Metal chlorides (MCl_4 , where M = Hf, Zr, or Ti) emit dense white fumes of HCl in humid air and with water and easily hydrolyze with formation of a series of metal hydroxychlorides: MCl_3OH , $\text{MCl}_2(\text{OH})_2$, $\text{MCl}(\text{OH})_3$, and $\text{M}(\text{OH})_4$ according to the following reactions:^{10–20}



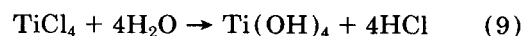
Hydrolysis of HfCl_4 and ZrCl_4 occurs to $\text{HfCl}_2(\text{OH})_2$ and $\text{ZrCl}_2(\text{OH})_2$, and after evaporation of water (at room temperature) are formed $\text{HfCl}_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ and $\text{ZrCl}_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ small, colorless, needle-like crystals (Fig. 1, Fig. 2).¹³ During the heating of these crystals at 70°C, HCl as well as water is given off and MOCl_2 and $\text{M}_2\text{O}_3\text{Cl}_2$ are formed according to reactions:



The dissociation of dried MOCl_2 and $\text{M}_2\text{O}_3\text{Cl}_2$ at about 110°C furnishes metal oxide (MO_2) and metal chlorides (MCl_4):



Hydrolysis of TiCl_4 occurs directly to $\text{Ti}(\text{OH})_4$:^{10,12,21,22}



and during the water evaporation in a form of white powder TiO_2 is formed (Fig. 3):

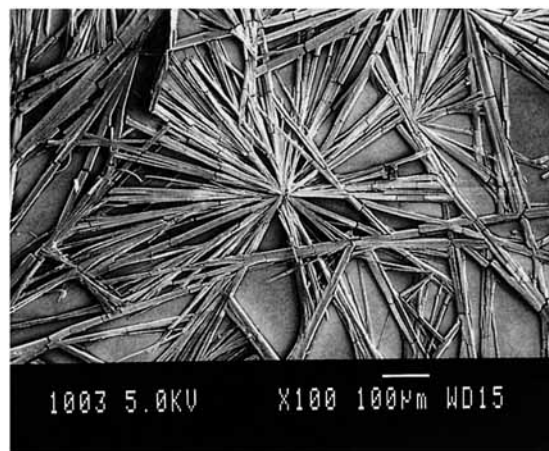


Figure 2 SEM photomicrograph of $\text{ZrCl}_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ crystals.

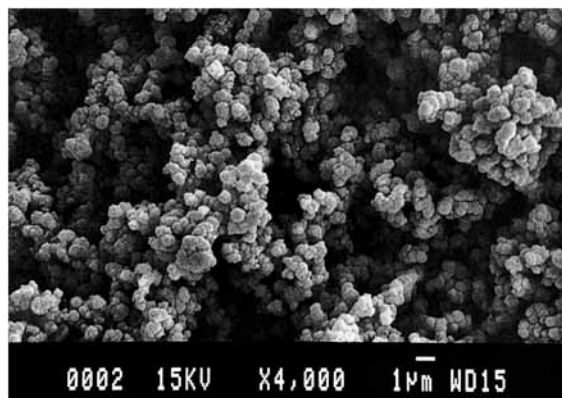
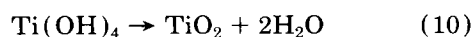


Figure 3 SEM photomicrograph of $\text{Ti(OH)}_4\text{—TiO}_2\text{·}2\text{H}_2\text{O}$ powder.



The IR spectra of hydrolysis products of MCl_4 (Fig. 4) are almost identical to these reported elsewhere.^{4,18–20} In the IR spectra the following peaks appear and can be assigned:^{23,24} 3397 cm^{-1} [Fig. 4(a)], 3406 cm^{-1} [Fig. 4(b)], 3400 cm^{-1} [Fig. 4(c)] (water band stretching vibration), and 1625 cm^{-1} [Fig. 4(a)], 1627 cm^{-1} [Fig. 4(b)], 1629 cm^{-1}

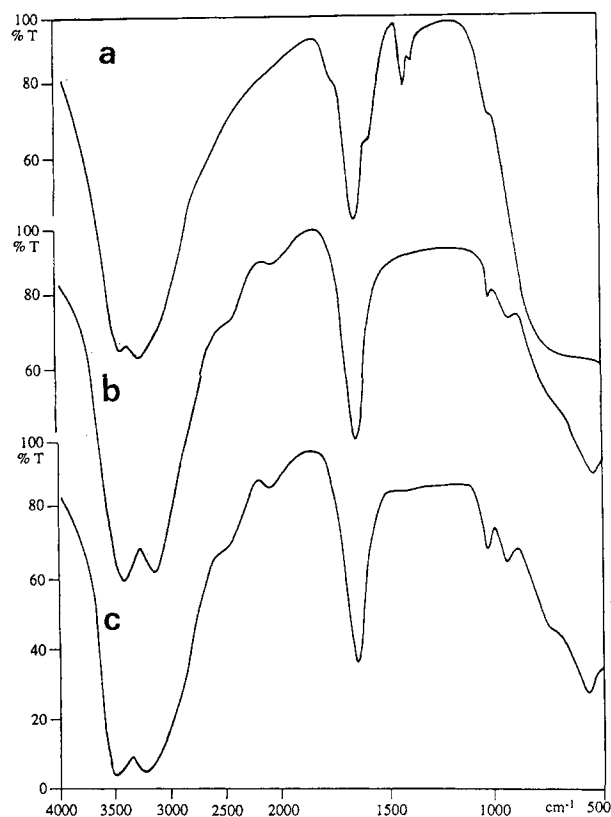


Figure 4 IR spectra of hydrolysis products of: (a) TiCl_4 , (b) ZrCl_4 , and (c) HfCl_4 .

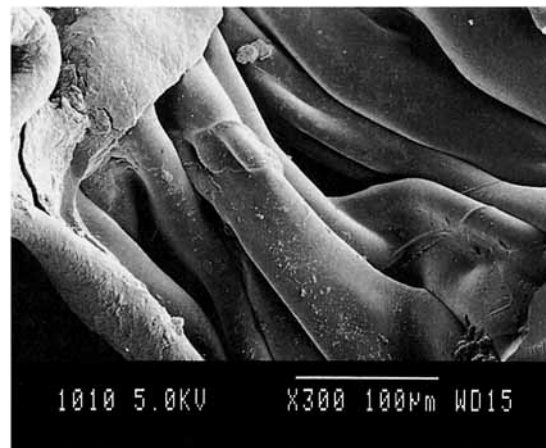


Figure 5 SEM photomicrograph of dried poly(acrylic acid) (PAA)-Hf(IV) gel, obtained at ratio PAA : HfCl_4 = 2 : 1.

[Fig. 4(c)] (water band bending vibration) indicate the presence of hydrated water in hydrolyzed metal salts. The bands at 3200 cm^{-1} [Fig. 4(a)], 3124 cm^{-1} [Fig. 4(b)], and 3144 cm^{-1} [Fig. 4(c)] belong to hydroxyl (OH) groups stretching vibrations in $\text{ZrCl}_2(\text{OH})_2$ [Fig. 4(b)], $\text{HfCl}_2(\text{OH})_2$ [Fig. 4(c)], and $\text{Ti(OH)}_4(\text{TiO}_2\text{·}2\text{H}_2\text{O})$ [Fig. 4(a)]. The band 1400 cm^{-1} [Fig. 4(a)] belongs to the hydroxyl groups bond to the titanium atoms of the surface of the gel. The broad strong band around 600 cm^{-1} [Fig. 4(a)] is due to the Ti—O—Ti bond vibration. The peaks 550 cm^{-1} [Fig. 4(b)] and 554 cm^{-1} [Fig. 4(c)] belong to the Zr—Cl and Hf—Cl bond vibrations.

Addition of poly(acrylic acid) (PAA) to the water solutions of MCl_4 causes precipitation of white, dense hydrogels (Fig. 5, 6, 7). Morphologically the PAA-Ti(IV) hydrogel (Fig. 7) differs significantly from PAA-Hf(IV) (Fig. 5) and PAA-Zr(IV) (Fig.

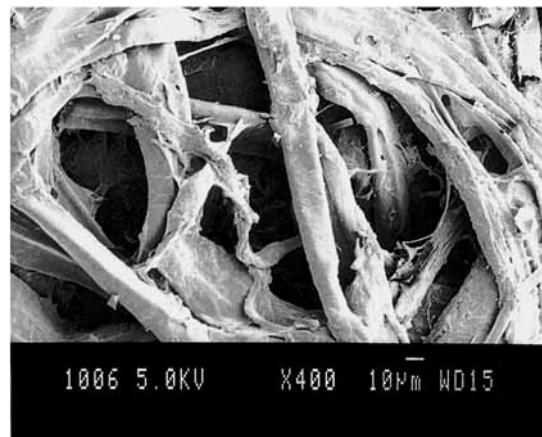


Figure 6 SEM photomicrograph of dried poly(acrylic acid)-Zr(IV) gel, obtained at ratio PAA : ZrCl_4 = 2 : 1.

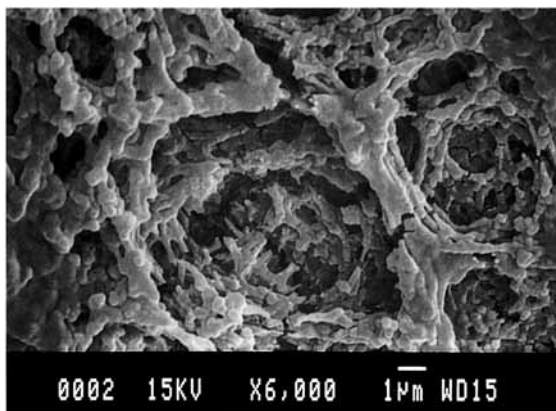


Figure 7 SEM photomicrograph of dried poly(acrylic acid)-Ti(IV) gel, obtained at ratio PAA : TiCl₄ = 2 : 1.

6) hydrogel structures, because it contains a large amount of embedded TiO₂ grains. Similar hydrogels are formed when PAA is added to HfCl₂(OH)₂ and ZrCl₂(OH)₂ water solutions. These PAA-M(IV) hydrogels are formed according to reactions:

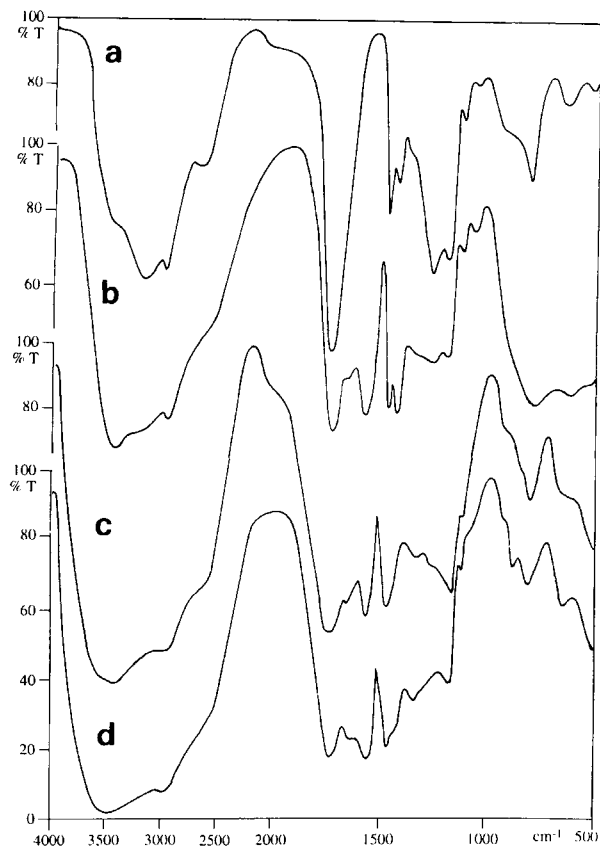


Figure 8 IR spectra of: (a) PAA, (b) PAA-Ti(IV), (c) PAA-Zr(IV), and (d) PAA-Hf(IV) gels, obtained at ratio PAA : MCl₄ = 2 : 1.

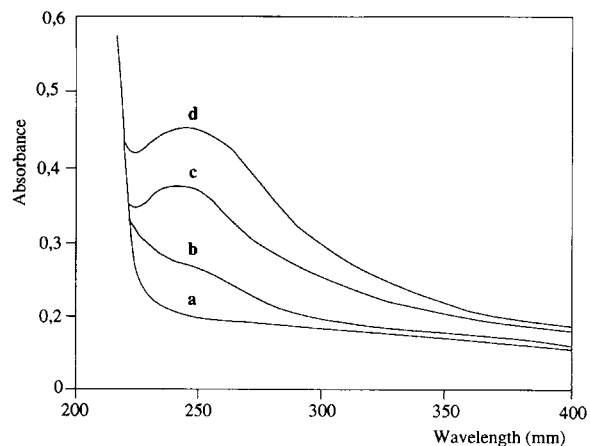
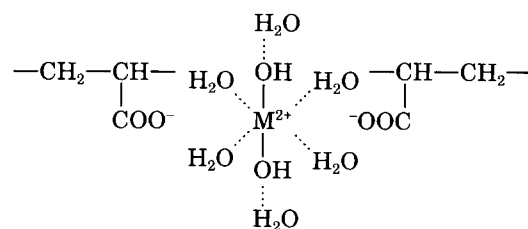
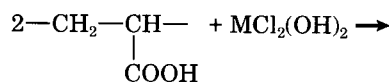
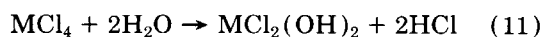


Figure 9 UV spectra of: (a) pure PAA, (b) PAA-Ti(IV), (c) PAA-Zr(IV), and (d) PAA-Hf(IV) water-swollen hydrogels, obtained at ratio PAA : MCl₄ = 2 : 1.



Elemental analysis does not show the presence of

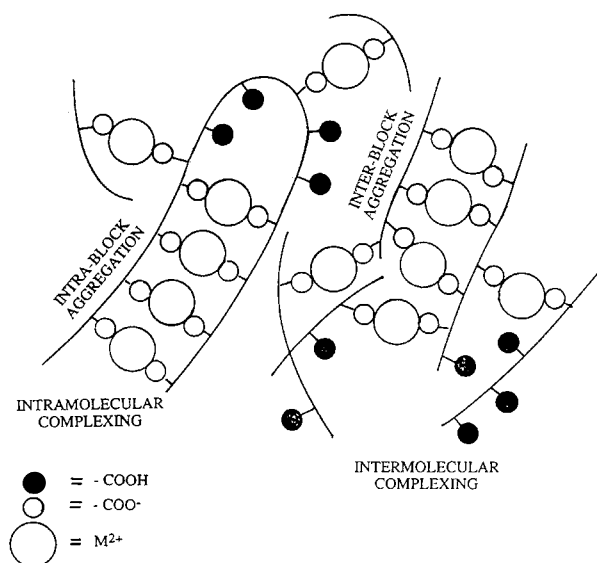


Figure 10 Probable mode of intra- and intermolecular complex formation between PAA and M(IV) chlorides.

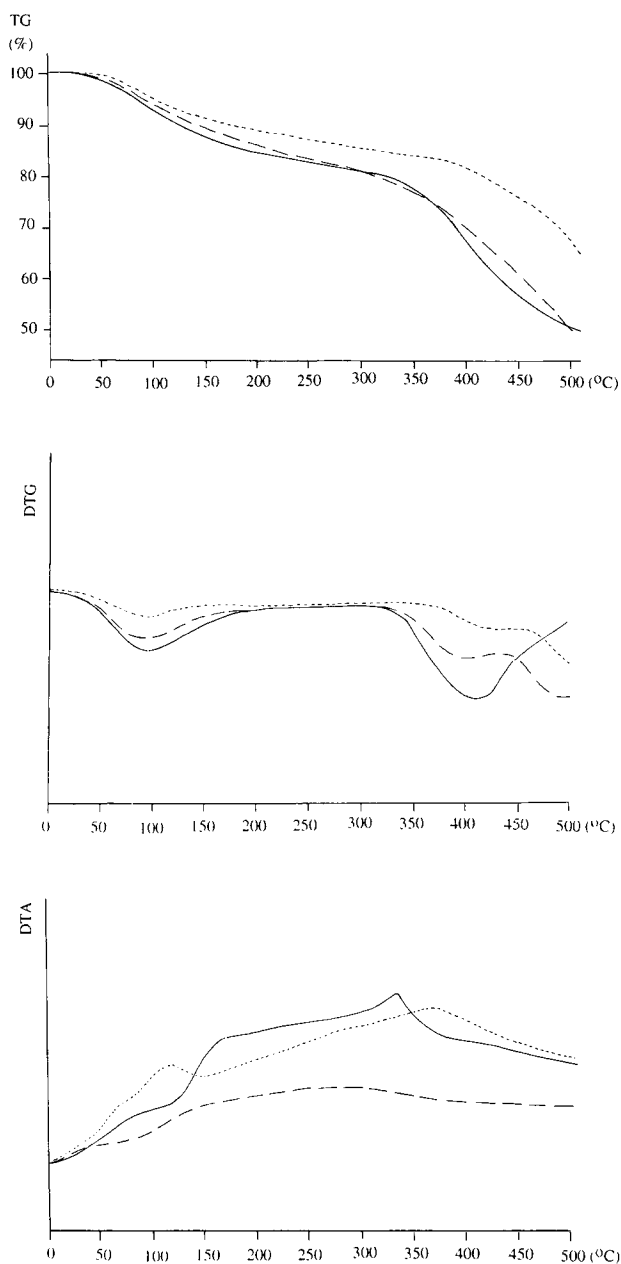


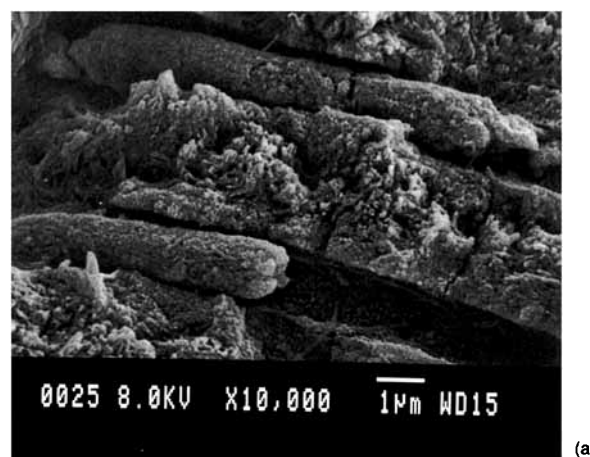
Figure 11 Thermogravimetric analysis curves: (a) TG, (b) DTG, and (c) DTA of poly(acrylic acid) PAA-M(IV) gels: (—) PAA-Ti(IV); (---) PAA-Hf(IV); and (- -) PAA-Zr(IV) gels, obtained at ratio PAA : $MCl_4 = 2 : 1$.

chlorine and coordinated HCl in PAA-M(IV) hydrogels. These gels retain about 90 wt % of water, and determination of coordination water is very difficult. Regarding the coordination number of the metals IV group, the coordination number of water in PAA-M(IV) hydrogels should be 6 or 8 molecules.

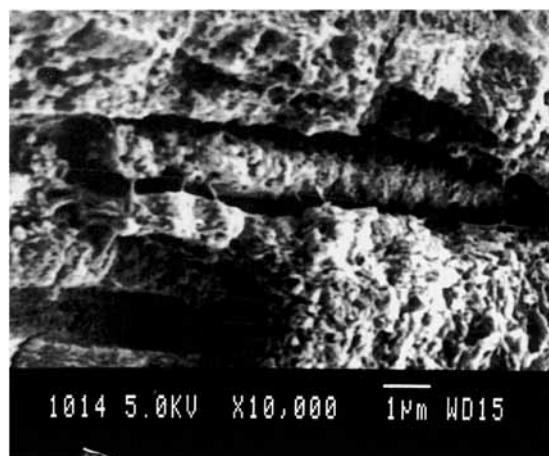
IR spectra of PAA-M(IV) hydrogels are shown in Figure 8. They exhibit a band at $1710\text{--}1730\text{ cm}^{-1}$ associated with the C=O asymmetrical stretching vibrations of carboxyl (COOH) groups in PAA [Fig.

8(a)]. The maximum of carboxyl groups which reacted with $MCl_2(OH)_2$ (reaction 12) was 30–40% (data obtained from the subtraction of FT-IR spectra). However, the amount of carboxyl groups reacted with $MCl_2(OH)_2$ depends on the concentration of the latter used. A new band at 1563 cm^{-1} (PAA-Ti(IV) [Fig. 8(b)]), 1542 cm^{-1} (PAA-Zr(IV) [Fig. 8(c)], and 1546 cm^{-1} (PAA-Hf(IV) [Fig. 8(d)], which belongs to asymmetrical vibrations of the ionized carboxyl group (COO^-),²⁵ appears. The broad bands $3400\text{--}3500\text{ cm}^{-1}$ and 1625 cm^{-1} belong to water band stretching and bending vibrations, respectively. The band at $3124\text{--}3144\text{ cm}^{-1}$ attributed to hydroxyl (OH) groups stretching vibrations in PAA-M(IV) hydrogels is strongly overlapped by the water band stretching vibration.

The UV spectra of PAA-M(IV) swollen hydrogels (Fig. 9) show formation of weak bands at 302 nm (PAA-Ti(IV) [Fig. 9(b)], 280 nm (PAA-



(a)



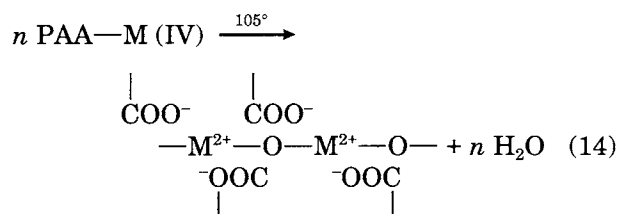
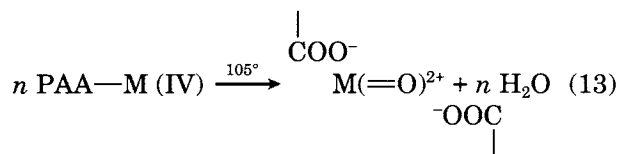
(b)

Figure 12 SEM photomicrographs of the dentin channels blocked (plugged) by: (a) PAA-Hf(IV) and (b) PAA-Zr(IV) hydrogels, obtained at ratio PAA : $MCl_4 = 2 : 1$.

Zr(IV) [Fig. 9(c)], and 290 nm (PAA-Hf(IV) [Fig. 9(d)], which belong to the $-\text{COO}^- \text{Me}^{2+} (\text{OH})_2 \text{OOC}-$ complex formed.

Probable mode of intra- and intermolecular complex formation between PAA and $\text{MCl}_2(\text{OH})_2$ is shown in Figure 10. The presence of molecular heterogeneity is due to randomly ordered intra- and/or intermolecular aggregations in PAA-M(IV) complexes. It is reasonable to set up a hypothesis that these complexes contain some relatively long sequences (blocks) of such aggregations which can retain up to 90% of swelled water. The heterogeneity distribution is considered to affect hydrogel properties.

The dried PAA-M(IV) hydrogels (at room temperature) lose their swelling capability and when placed in water, they retain only 30–40 wt-% of water, whereas, when dried at 105°C they form non-swelling powders. The thermogravimetric analysis (Fig. 11) indicates that at about 90°C all complexed water is removed and above 300°C thermal degradation of samples occurs (samples become brown-black colored). During the heating (at 105°C) of PAA-M(IV) hydrogels, the probable changing of their structure occurs and from hydroxyl groups (OH) bounded to M(IV) water and new types of metal oxide chains $-\text{M}(=\text{O})^{2+}$ [reaction (13)] and/or $-\text{O}-\text{M}^{2+}-$ [reaction (14)] can be formed:

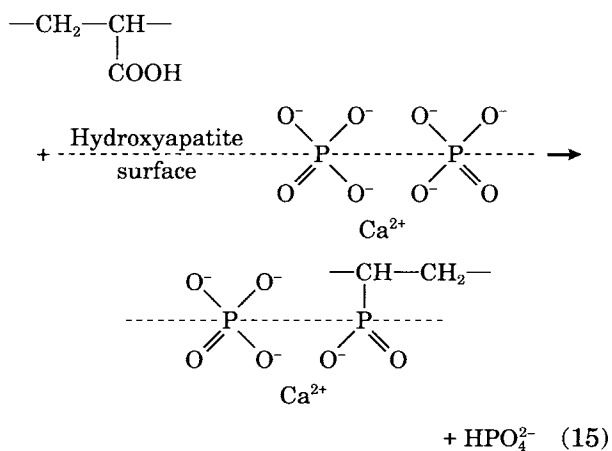


The metal-oxygen groups gives rise to the following IR active vibrational modes. The intense narrow absorption band at 800–1000 cm^{-1} associated with the presence of $\text{M}=\text{O}$ groups and the broad band over the range 840–970 cm^{-1} attributed to the presence of $-\text{M}-\text{O}-$ type chains. The symmetric $\text{M}-\text{O}$ stretch and the asymmetric $\text{M}-\text{O}$ stretch appear at 570–630- cm^{-1} bands, respectively. The heated PAA-Ti(IV) hydrogel shows the presence of $\text{M}=\text{O}$ structures whereas PAA-Hf(IV) and PAA-Zr(IV) show $-\text{M}-\text{O}-$ chains.

Formation of white, colorless PAA-M(IV) hydrogels was very attractive for the plugging of chan-

nels in the enamel and dentin of the human teeth. For tightening procedure, cross sections of cut teeth were exposed first to 3–5 wt % of $\text{MCl}_2(\text{OH})_2$ water solutions. After draining and cleaning with filter paper, the samples were exposed for next 5 min into 5 wt % of PAA in water solution. SEM photomicrographs [Fig. 12 (a), (b)] show that teeth channels are well tightened by PAA-Hf(IV) [Fig. 12(a)] and PAA-Zr(IV) [Fig. 12(b)] hydrogels. The PAA-Ti(IV) is useless for tightening of teeth channels because it contains embedded TiO_2 powder (Fig. 7) which blocks entrances of tubules. Blocking of channels by PAA-Hf(IV) and PAA-Zr(IV) hydrogels has a tremendous effect on the flow of water through dentine (samples cut from the same tooth) (Fig. 13). The rapid decrease in the hydraulic permeability after blocking of channels during the first 10 min was followed by a slower decrease for the next 200 min. This is probably due to delayed gelation that depends on the diffusion of both $\text{MCl}_2(\text{OH})_2$ and PAA through microscopic channels. It might also depend on the compression of the formed hydrogel in narrow parts of the channels due to fluid pressure. Hydraulic permeability after blocking differs remarkably, depending on the tooth sample, its morphology, age, and origin. For that reason permeability results are only comparable when cross sections for measurements were made from the same tooth.

The presence of free carboxyl groups in PAA-M(IV) hydrogel is an advantage from the dental point of view. These groups in PAA either form a strong ionic bond to the calcium ions on the surface of apatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) (a basic component of tooth enamel and dentine)²⁶ or displace phosphates from the apatite surface:^{27,28}



Our development of tooth plugging by PAA-metal salt complexes may have practical implications on dentinal hypersensitivity and caries.

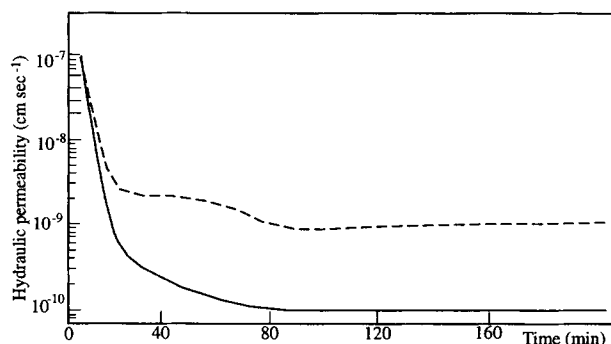


Figure 13 Kinetic curves of the hydraulic permeability of water through channels in the dentin blocked with: (---) PAA-Zr(IV) and (—) PAA-Hf(IV) hydrogels, obtained at ratio PAA : MCl_4 = 2 : 1.

CONCLUSIONS

On the basis of results obtained we can conclude that hydrogels formed during the reaction of poly(acrylic acid) (PAA) with $HfCl_4$ and $ZrCl_4$ in water solution have the same structures. Two carboxylic groups are involved in the complex formation with $M(OH)_2^{2+}$ ion. Gels are crosslinked by ionic type bonds and can retain up to 90% of water. Under heating PAA-M(IV) hydrogels lose coordination water and new types of metal-oxygen chains are probably formed. The PAA-Hf(IV) and PAA-Zr(IV) hydrogels have the ability to plug channels in the human teeth and cause the decrease of fluid transportation through these.

Authors gratefully acknowledge the support of the Swedish Institute, who generously provided a post-doctorate stipend, thus enabling Dr. Halina Kaczmarek to play a major role in this research. This work was supported by the Swedish Medical Research Council (project No B93-24B-09953-02B).

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Received March 6, 1995

Accepted November 19, 1995