Structures and Mechanisms of Formation of Poly(Acrylic Acid)-Iron(II and III) Chloride Gels in Water and Hydrogen Peroxide

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SYNOPSIS

Poly(acrylic acid) (PAA) can form stable and insoluble gels with $FeCl_3$ in water or in H_2O_2 (30 wt %). Two carboxylic groups are complexed by the $FeCl^{2+}$ ion. $PAA-FeCl_3$ (2 : 1) gels have found practical application in the blocking of microscopic channels in tooth dentin and thereby decrease the fluid permeability and protect against tooth decay. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(acrylic acid) (poly(propenoic acid)) (PAA) forms gels on the addition of inorganic salts such as Ca^{2+}, Cu^{2+}, Ni^{2+}, and Mg^{2+} chlorides, and Fe^{2+} [$FeSO_4 \cdot H_2O$, $Fe(NH_4)_2(SO_4)_2$,[1-3] Fe^{3+}[$FeCl_3$, $Fe(NO_3)_3 \cdot 9H_2O$].[4,5] Little is known of the structures of PAA–iron salt gels. However, there are several practical applications such as: hemostatic pharmaceuticals (known as "Feracryls");[1,6] antimicrobial agents (to suppress the growth of *Staphylococus, Escherichia coli, Pseudomonas aeruginosa*, and *Proteus* strains),[7] and plant (Fe) fertilizers (to decrease the iron deficiency in plants).[8,9]

It is also well known that PAA and a number of other poly(alkenoic acids) react with aluminosilicates giving glass–ionomer cements widely used in dentistry.[10] A serious disadvantage of ionomer glasses is that they contain aluminum. They are easily decomposed by acids. Aluminum can enter the silica network that then becomes basic and susceptible to attack by hydrogen ions from the acids.

Human teeth contain microdiameter channels (Fig. 1) in the enamel and dentin, filled with natural biohydrogel that plays an important role in the transportation of ions.[11] In the dentin channels (tu-bules) there are also pathways for the penetration of bacteria during tooth decay (caries).

Glass–ionomer cements have no ability to penetrate through these channels because the tubules are filled with biohydrogel in which they are insoluble and undiffusable. On the other hand glass–ionomer cements are easily decomposed by acids, which limits the lifetime of such tightenings. We have found that it is possible to obliterate these channels by using PAA–iron salts gels. Both iron salts and PAA easily penetrate (diffuse) through the biohydrogel in tubules and when in contact with each other form insoluble gels that can reduce the transportation of water, ions, and bacteria through the dentinal tubules.

The reason for this work was to study the chemical structure of PAA–iron(II and III) chloride gels and the mechanism of gel formation in water and in hydrogen peroxide solution (30 wt % is applied in dentistry[12]).

EXPERIMENTAL

PAA (Aldrich; molecular weight, 5000, average of 70 carboxylic groups per molecule); iron(II) chloride tetrahydrate [($FeCl_2 \cdot 4H_2O$), Merck]; and iron(III) chloride anhydrous [($FeCl_3$), Merck] were used without further purification. Hydrogen peroxide (H_2O_2 solution in water, 30 wt %, Aldrich) was used as received.
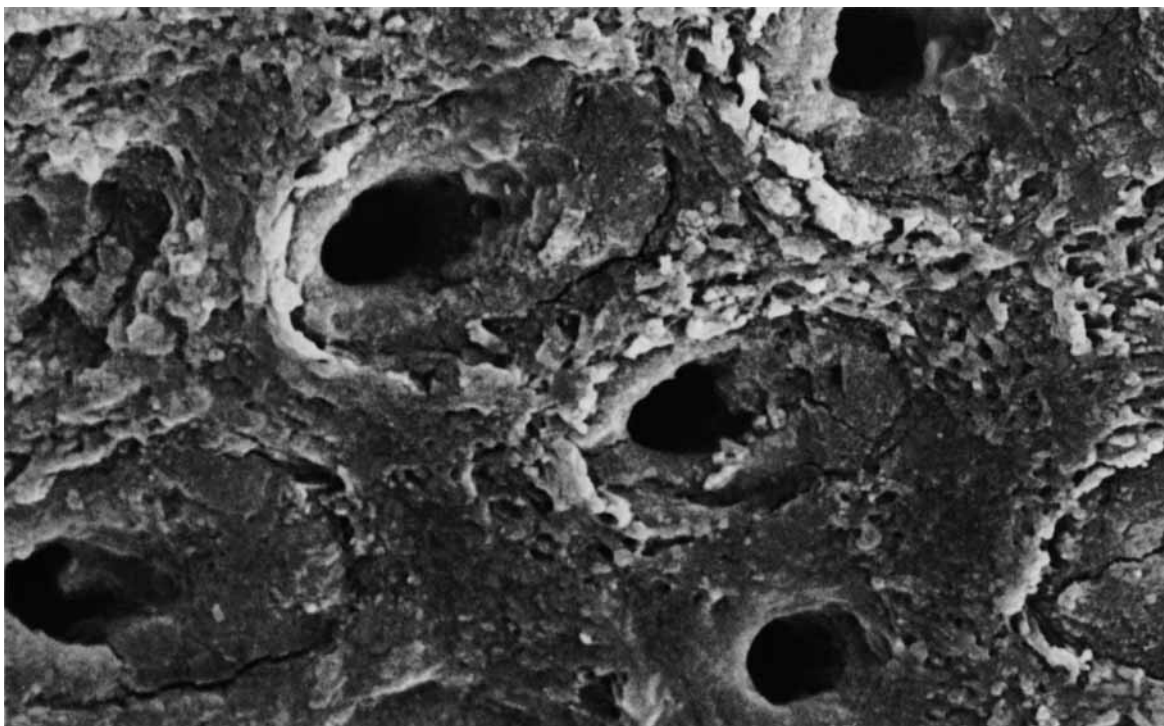

Figure 1 SEM photomicrograph of channel entrances into the tooth dentin. Scale bar 1 μm (photograph by E. Adamczak and J. F. Rabek).

For gel preparations, a 5 wt % distilled water solution of PAA and $FeCl_3$ or $FeCl_2$ separately, and 5 wt % solution of PAA in H_2O_2 30 wt % were used. The following abbreviations are used in this work for the gels obtained: in water PAA-$FeCl_3$ (100 : 1) (G-IA); (10 : 1) (G-IB); (2 : 1) (G-IC); in H_2O_2 30 wt %: PAA-$FeCl_3$ (100 : 1) (G-IIA); (10 : 1) (G-IIB); (2 : 1) (G-IIC); and PAA-$FeCl_2$ (100 : 1) (G-IIIA); (10 : 1) (G-IIIB); (2 : 1) (G-IIIC).

UV-vis and IR spectra were recorded with a Beckman 7500 UV-vis and an FT-IR Perkin–Elmer 1650 spectrometers, respectively. UV-vis spectra of thin layers of swollen hydrogels were made on the surface of a quartz cuvette, whereas IR spectra were measured from the dry gels dispersed in KBr pellets.

DSC measurements were made on powdered 3.0 ± 0.1 mg samples in covered aluminum pans using the Perkin–Elmer DSC4 thermal analysis system.

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 hydrogel.

The HCl formed in the reaction between PAA and $FeCl_3$ (after removing gel) was titrated with 0.01M NaOH to pH 7.0. The chlorine content in dry gels was determined by a routine method described elsewhere.[13]

The transportation of water through channels in teeth was measured with a device constructed by L. A. Lindén and Ö. Källskog in our institute. Planoparallel sections of a tooth (210–240 μm) were prepared according to a standard procedure, and placed as membranes in a two-chamber diffusion cell device (Fig. 2). Smear layers were removed by a 5-s wash with ethylenediaminetetraacetic acid (EDTA) (5 wt %). One chamber was connected to a servo-nulling pressure device and a Landis mercury manometer; the second to a high precision capillary (Fig. 3). By changing the hydrostatic pressure on one side of the tooth membrane, the hydraulic pressure flow could be registered as the meniscus movements, using a microscope connected to a video recording system (Ikegami, Japan) that consists of a video camera (type ICD-40 CCD), a monitor (type PM-930), and a time/date generator and counter for superimposed images (type TD-85).

Sound deciduous and permanent dentin sections were subjected to different hydrostatic pressures (25–50 mmHg) to register the hydrostatic flow. After
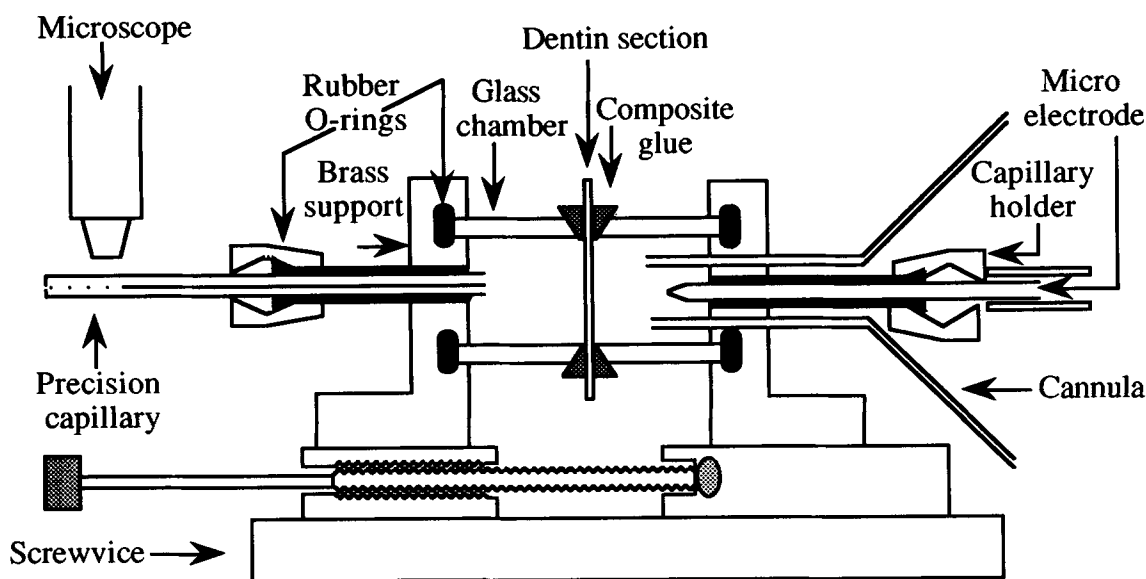
Figure 2 A design of a two-chamber diffusion cell.

draining one chamber (Fig. 2), 10 μL of FeCl$_3$ 5 wt % in distilled water was introduced and allowed to diffuse into a biohydrogel in dentinal tubules for 5 min. After draining and cleaning with filter paper, the dentinal membrane was treated with a PAA 5 wt % water solution for another 5 min. After thoroughly rinsing with water, the hydraulic permeability measurements were performed for periods up to 1 month.

This two-chamber, microdiffusion cell device can also be used in any study of liquid flow through other polymeric membranes in a microscale application.

RESULTS AND DISCUSSION

Addition of FeCl$_3$ (in solid powder or in 5 wt % water solution) to PAA 5 wt % in water or to H$_2$O$_2$
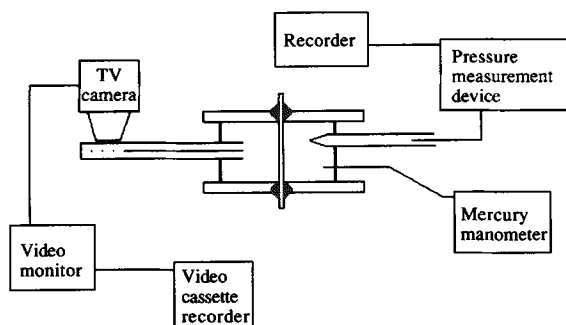

Figure 3 Device for measuring liquid flows through the tooth membrane (dentin section).

30 wt %) causes rapid precipitation of stable and insoluble hydrogel complexes containing 90–100% water (G-I and G-II, respectively).

The FeCl$_2$ (if it is free from Fe^{3+} ions) does not give any gel with PAA dissolved in water. However, a gel (G-III) is rapidly formed between FeCl$_2$ and PAA dissolved in H$_2$O$_2$ 30 wt %.

All gels (G-I, G-II, and G-III) are insoluble in water and organic solvents. They are, however, destroyed in concentrated HCl, leaving an insoluble, swollen PAA. Complexes between PAA and FeCl$_3$ do not form in a concentrated HCl solution. All of these intermolecular complexes are formed by the association of different molecular chains through secondary ionic binding forces. These systems are interesting because acrylic acid and methacrylic acid units are known to interact with each other through hydrogen bonding and dipole interactions,[14] and these units are also known to form metal–polymer complexes with transition metal ions.[15–20]

All gels remain swollen in water for an unlimited time. They can be dried to zero water content (below 105°C) to give glassy materials, which can be ground to yellow-brown powders. Dried gels do not swell again in water.

The SEM micrographs show that swollen gels G-I, G-II, and G-III have spongy structures with twisted "fiber-like" structures (Fig. 4). This structure can be well seen in dryed gels by the liophilization procedure.

The glass-transition temperatures (T_g) determined for pure PAA used in this work compares
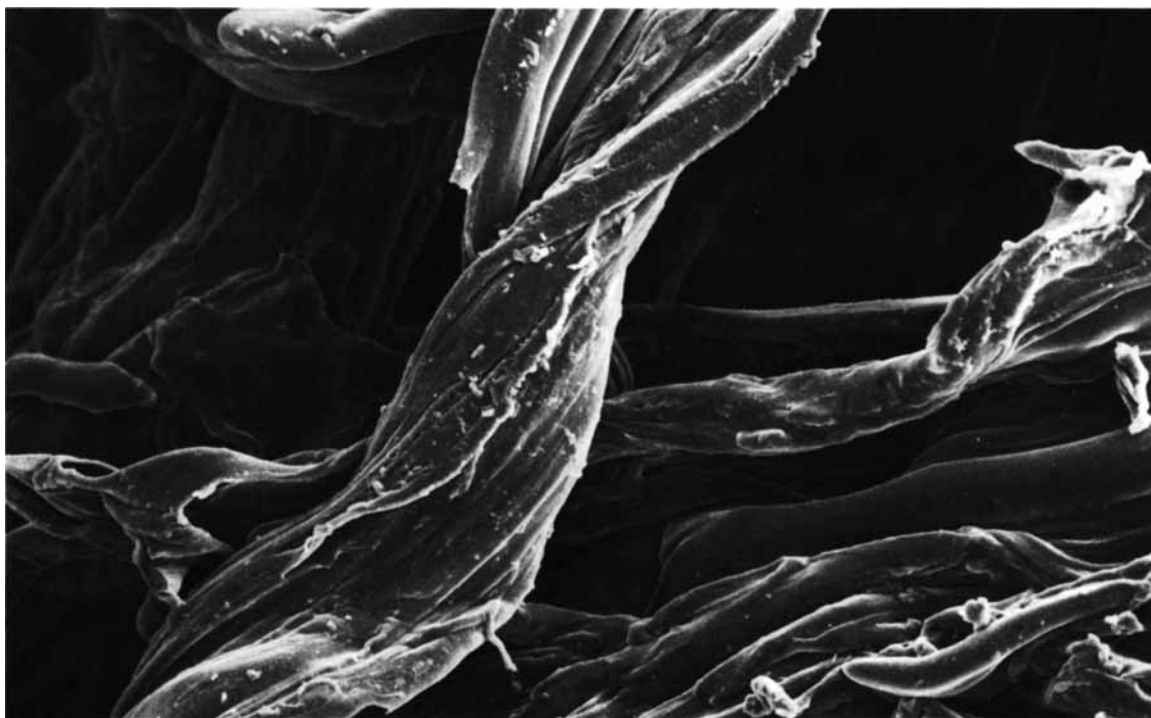
Figure 4   SEM photomicrograph of dried poly(acrylic acid)-FeCl₃ (2 : 1) gel (G-IC). Scale bar 100 μm (photograph by E. Adamczak and J. F. Rabek).

favorably with previously published results.[21] The T_g obtained for gels G-IA and G-IB are 118°C and 148°C, respectively. The gel G-IC did not exhibit any T_g probably because of the very high density of the crosslinks. The T_g for gels G-II and G-III are almost the same as for G-I. The problem with the glass transition in PAA is that its values diverge between 88°C and 166°C. The dehydration of PAA and anhydride formation increase the T_g drastically.[22] Drying of the gels may also cause their dehydration. On the other hand, formation of PAA-FeCl₃ complexes causes not only crosslinking of macromolecules, but simultaneously decreases the amount of carboxylic groups that can be dehydrated. This makes it difficult to interpret T_g changes observed for gels G-I, G-II, and G-III.

The width of the carboxyl band at 3500–3000 cm⁻¹ in IR spectra indicates that carboxyl acids exist normally in dimeric forms with very strong hydrogen bridges between the carbonyl and hydroxyl groups of the two molecules (in the form of dimers).[23] The abnormally strong hydrogen bonding in the solid PAA makes the O — H stretching vibrations so distorted from the normal as to be characteristic. The

main peak of the OH absorption in PAA is at 3103 cm⁻¹ with a main satellite band at 2650 cm⁻¹ [Fig. 5(a–c)]. The absorption between 2700–2500 cm⁻¹ is strong evidence for the presence of dimeric carboxylic acid because it is characteristic only in a strongly bonded OH group. Although bonds of this strength are unusual in polymers other than poly(carboxylic acids).

The PAA shows a strong band at 1711 cm⁻¹ associated with the C=O antisymmetrical and a weaker band at 1420 cm⁻¹ with the symmetrical stretching vibrations. At 1240 cm⁻¹ the band in PAA appears, which results from the coupled C — O and OH in-plane deformation modes. Specifically, syndiotactic PAA has a strong characteristic band at 1240 cm⁻¹, whereas the 930 cm⁻¹ band is attributed to the isotactic form and splits into two bands at 1215 and 1275 cm⁻¹.[24,25]

The IR spectra of PAA used in this work [Fig. 5(a–c)] show that the polymer sample probably has the syndiotactic configuration. Studies on thermal characteristics of the atactic PAA have shown that upon heating new bands at 1806, 1757, and 1030 cm⁻¹ simultaneously appear in the IR spectra. These
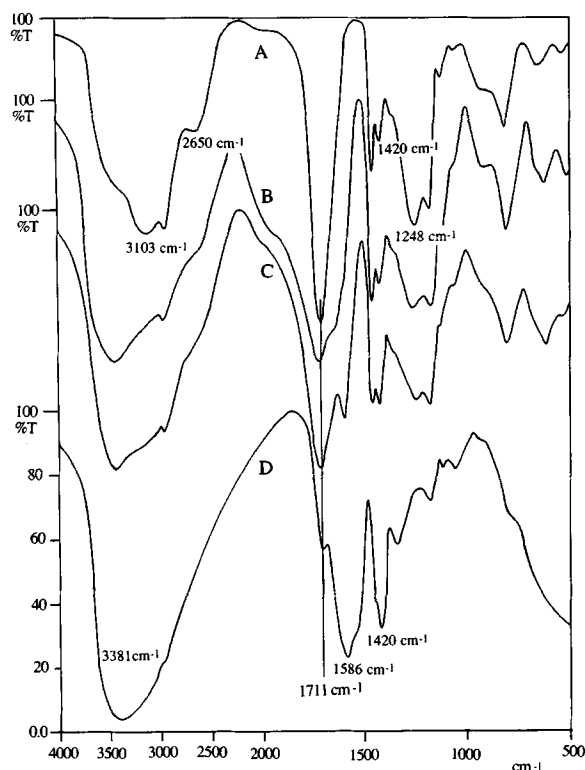
Figure 5(a)   IR spectra of poly(acrylic acid)-$FeCl_3$ gels obtained in H_2O: (A) pure poly(acrylic acid) (PAA); (B) PAA-$FeCl_3$ (100 : 1) (G-IA); (C) PAA-$FeCl_3$ (10 : 1) (G-IB); and (D) PAA-$FeCl_3$ (2 : 1) (G-IC).

bands indicate a formation of anhydride from carboxylic acid.[22,26]

Figures 5(a-c) show the change of IR spectra of PAA during the formation of gels with $FeCl_3$ [G-I, Fig. 5(a)], $FeCl_3$ in H_2O_2 [G-II, Fig. 5(b)], and $FeCl_2$ in H_2O_2 [G-III, Fig. 5(c)] at different molar ratios of PAA : Fe salts. Analysis of these spectra shows that hydrogen-bonded carboxyl bands at 3103, 2650, 1711, and 1248 cm^{-1} disappear in the reaction with Fe-salts, and a new band characteristic for the formation of ionized carboxyl groups (complexed with $FeCl^{2+}$) at 1586 cm^{-1} [G-I, Fig. 5(a)], 1592 cm^{-1} [G-II, Fig. 5(b)] and 1592 cm^{-1} [G-III, Fig. 5(c)] appears. The band around 1590 cm^{-1}, which is characteristic for the antisymmetrical vibrations of the ionized carboxyl group, COO^-, is accompanied by the band increasing at 1420 cm^{-1} [G-I, Fig. 5(a)], 1425 cm^{-1} [G-II, Fig. 5(b)], and 1421 cm^{-1} [G-III, Fig. 5(c)], which belongs to the symmetrical vibration of the ionized carboxyl group, COO^-. At the same time, a band formed at 3381 cm^{-1} is characteristic for the free stretching vibrations of OH in carboxylic groups. It is evident from IR spectra [Fig.

5(a-c)] that the structure of PAA-iron salt complexes in the gels G-I, G-II, and G-III is almost the same.

The characteristic band for the CH_2 group in PAA at 2960 cm^{-1} and 2853 cm^{-1}, corresponding to the in-phase and out-of-phase stretching vibrations of the hydrogen atoms, are overlapped by the strong, broad carboxyl band. At 1455 cm^{-1} the absorption due to hydrogen bending vibrations in CH_2 appears, whereas skeletal vibration of the C — COOH forms at 1172 cm^{-1}. At 802 cm^{-1} a band from a rocking mode of the CH_2 group arises, which is not strictly a skeletal mode. Other weak absorption bands due to the skeletal vibrations appear in the region below 650 cm^{-1}. The data on which these assignments are based, were published previously for acrylic acid[27] and PAA.[24,25,28] The IR spectra of $FeCl_2$ and $FeCl_3$ lies in the far IR (600-20 cm^{-1}).[29] Increasing the band at 600 cm^{-1} [Fig. 5(a-c)] can be attributed to the Fe — Cl vibrational modes at the $FeCl^{2+}$ ion.[30]

The association of the Fe^{3+} (ferric) ion with chloride ions in water solution at pH 1, excluding the hydration of the metal and complex ions, is as follows[31]:
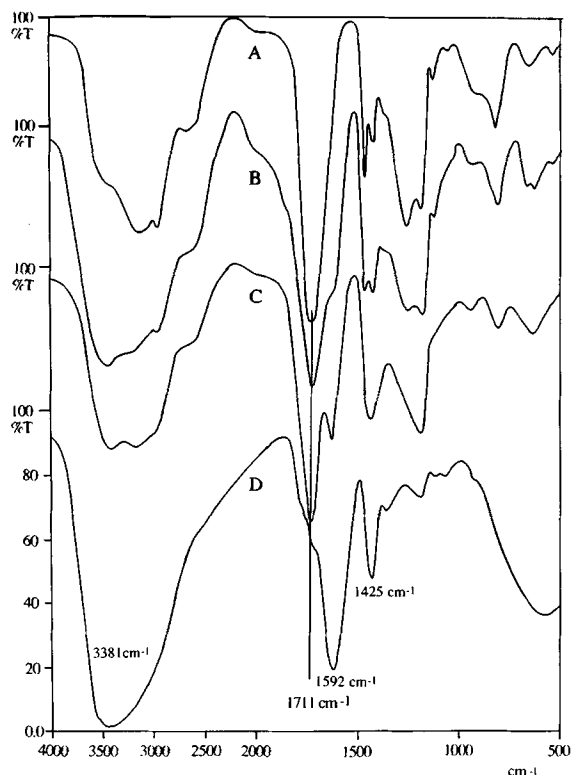

Figure 5(b)   IR spectra of poly(acrylic acid)-$FeCl_3$ gels obtained in H_2O_2: (A) pure poly(acrylic acid) (PAA); (B) PAA-$FeCl_3$ (100 : 1) (G-IIA); (C) PAA-$FeCl_3$ (10 : 1) (G-IIB); and (D) PAA-$FeCl_3$ (2 : 1) (G-IIC).
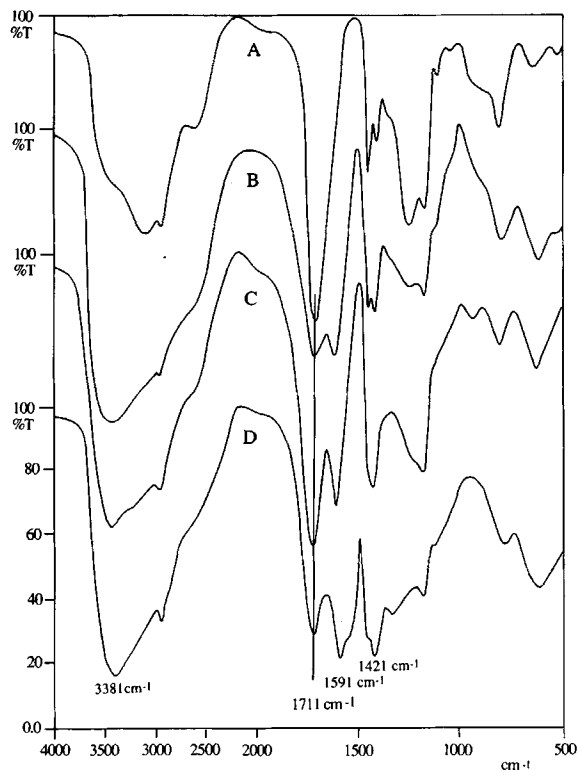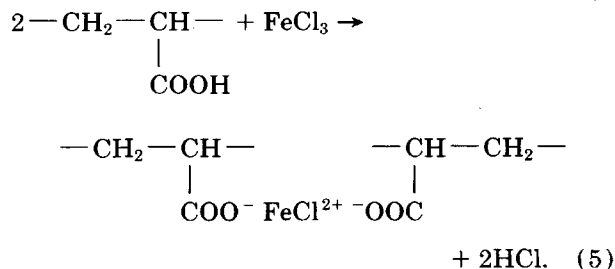
Figure 5(c)   IR spectra of poly(acrylic acid)-$FeCl_2$ gels obtained in H_2O_2: (A) pure poly(acrylic acid) (PAA); (B) PAA-$FeCl_3$ (100 : 1) (G-IIIA); (C) PAA-$FeCl_2$ (10 : 1) (G-IIIB); and (D) PAA-$FeCl_2$ (2 : 1) (G-IIIC).

$$Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+} \tag{1}$$

$$FeCl^{2+} + Cl^- \rightleftarrows FeCl_2^+ \tag{2}$$

$$FeCl_2^+ + Cl^- \rightleftarrows FeCl_3 \tag{3}$$

$$FeCl_3 + Cl^- \rightleftarrows FeCl_4^-. \tag{4}$$

Solutions of ferric chloride in water contain, in addition to the chloro-complexes, the hydroxy-complexes: $Fe(OH)^{2+}$, $Fe(OH)_2^+$, and $Fe(OH)_3$ that have been extensively investigated.[32,33] The absorption by the hydroxy-complexes is sufficiently large to interfere with the spectra of the chloro-complexes, even when the former are present in very small quantities.[32] Increase of pH causes formation of different iron hydroxy-complexes such as $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_4^+$, and $Fe(OH_3)_3$,[34-36] which causes additional complications of the investigated system. In addition to these problems, PAA becomes uncoiled at pH < 3, and exists as a PAA-salt.[37,38]

During the PAA reaction with $FeCl_3$ in water, HCl is produced, which causes strong acidity of the solution (pH 1). Titration values of the evolved HCl are shown in Figure 6. The double logarithmic plot

yields a straight line within experimental error for the measured HCl, which fits well with the amount of HCl calculated (broken line in Fig. 6) for the reaction in which two carboxylic groups are involved in the reaction with $FeCl_3$:

$$2 - CH_2 - \underset{\underset{COOH}{|}}{CH} - \; + FeCl_3 \rightarrow$$

$$- CH_2 - \underset{\underset{COO^- \; FeCl^{2+} \; {}^-OOC}{|}}{CH} - \qquad - \underset{|}{CH} - CH_2 -$$

$$+ 2HCl. \tag{5}$$

Elemental analysis for Cl in gels G-IC, G-IIC, and G-IIIC gave the following Cl content: 14.8, 9.6, and 6.9%, respectively, in comparison to the 16.6% calculated from the empirical formula $(C_3H_3O_2)_2FeCl$. Considering that 16.6% Cl is equivalent to two COOH groups involved in the reaction with one
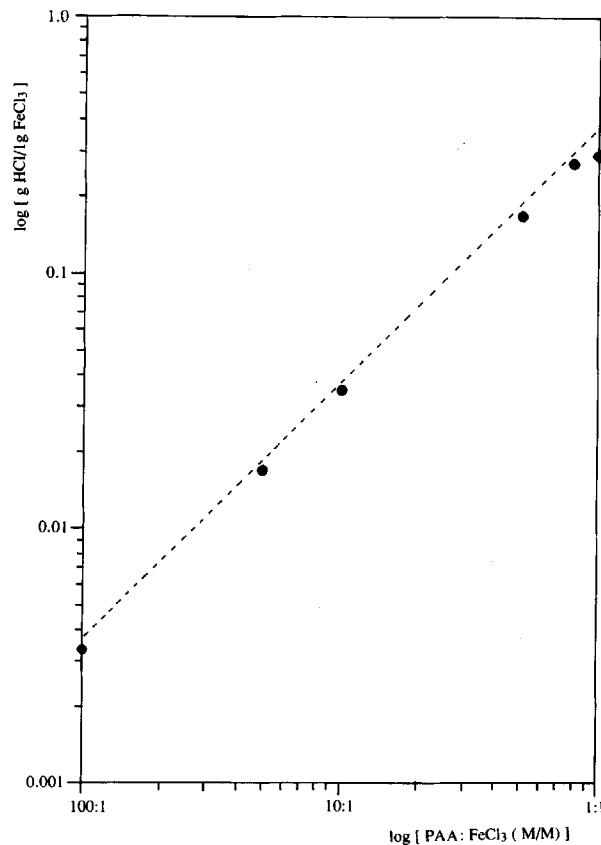

Figure 6   Titration data for the HCl formed in reactions between poly(acrylic acid) (PAA) and $FeCl_3$ in (●) water and (- - -) theoretical calculated data for the HCl involved in reaction (5).
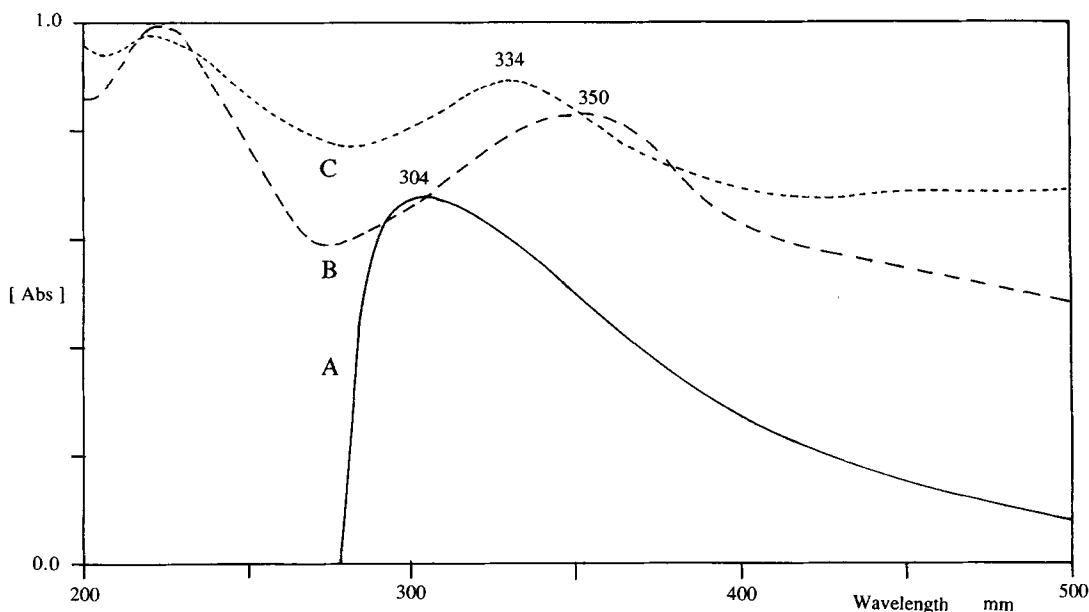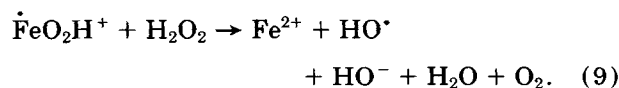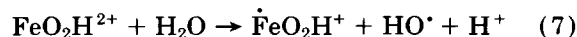
Figure 7 UV-vis absorption spectra of: (A) $FeCl_3$ ($1 \times 10^4 M$ in water); (B) poly(acrylic acid)-$FeCl_3$ (2 : 1) gel (G-IC); and (C) poly(acrylic acid)-$FeCl_2$ (2 : 1) gel (G-IIIC).

molecule of $FeCl_3$, the results show that 14.8 (G-IC), 9.6 (G-IIC), and 6.9% (G-IIIC) are equivalent to 1.78 (89%), 1.15 (57.5%), and 0.83 (41.4%) of COOH groups involved in the reaction of PAA with Fe-salts. The IR spectra show that the maximum of carboxyl groups involved in the reaction of PAA with $FeCl_3$ (2 : 1) are 64–70% in water (G-IC) and 60% in H_2O_2 30 wt % (G-IIC), whereas 40% are involved in the reaction of PAA with $FeCl_2$ (2 : 1) in H_2O_2 30 wt % (G-IIIC). These results are in a good agreement with the elemental analysis of Cl contents in gels G-IC, G-IIC, and G-IIIC.

UV-vis absorption spectrum of PAA-$FeCl_3$ (2 : 1) (G-IC) complex in the water swollen layer (Fig. 7) shows the presence of a broad absorption band with the maximum at 350 nm, characteristic for the presence of $FeCl^{2+}$ ions (λ_{max} at 340 nm).[31] A very similar absorption spectrum has been obtained for PAA-$FeCl_2$ (2 : 1) (G-IIIC) complex obtained in H_2O_2 30 wt % (Fig. 7). The $FeCl_3$ dissolved in water exhibits a band at 304 nm (Fig. 7). These results show that the complexed ion in PAA-Fe salts gels is the ion $FeCl^{2+}$ that complexes two COO^- ions [reaction (5)]. The Fe^{3+} cations probably do not form a gel complex with PAA. This is a reason why PAA does not react with $FeCl_3$ in concentrated HCl solution, where only Fe^{3+} ions exist. However, Fe^{3+} ions react with PAA in dimethyl formamide, giving polyion soluble complexes.[39,40] Polyethers form with $FeCl_3$ liquid complexes.[41] In polyelectrolytes the

complexation is often a function of the spacing of the reactive groups. Thus stereospecific isomers of PAA should probably show differences in their complexing capability due to differences in spacing on their side groups. Theoretically, $FeCl^{2+}$ ion can form intramolecular and/or intermolecular complexes with two carboxyl groups attached to one or two PAA molecules, respectively (Fig. 8). It is, however, less probable that $FeCl^{2+}$ can form a complex with two neighboring carboxyl groups in the same PAA molecule due to steric hindrances. Very strong ionic complexation forces probably cause the twisting of PAA molecules, which can be observed on the SEM micrograph of the PAA-$FeCl_3$ gel (G-IC) (Fig. 4).

Rapid and exothermic reaction of $FeCl_3$ with H_2O_2 occurs by the following mechanism[42–44]:

$$Fe^{3+} + H_2O_2 \rightarrow FeO_2H^{2+} + H^+ \qquad (6)$$

$$FeO_2H^{2+} + H_2O \rightarrow \dot{F}eO_2H^+ + HO^{\bullet} + H^+ \qquad (7)$$

$$Fe^{3+} + H_2O + HO^{\bullet} \rightarrow \dot{F}eO_2H^+ + 2H^+ \qquad (8)$$

$$\dot{F}eO_2H^+ + H_2O_2 \rightarrow Fe^{2+} + HO^{\bullet}$$
$$+ HO^- + H_2O + O_2. \qquad (9)$$

Ferrous ions (Fe^{2+}) formed in Reaction (9) are immediately oxidized to ferric ions (Fe^{3+}) by the Haber–Weiss rapid and exothermic reaction[42]:
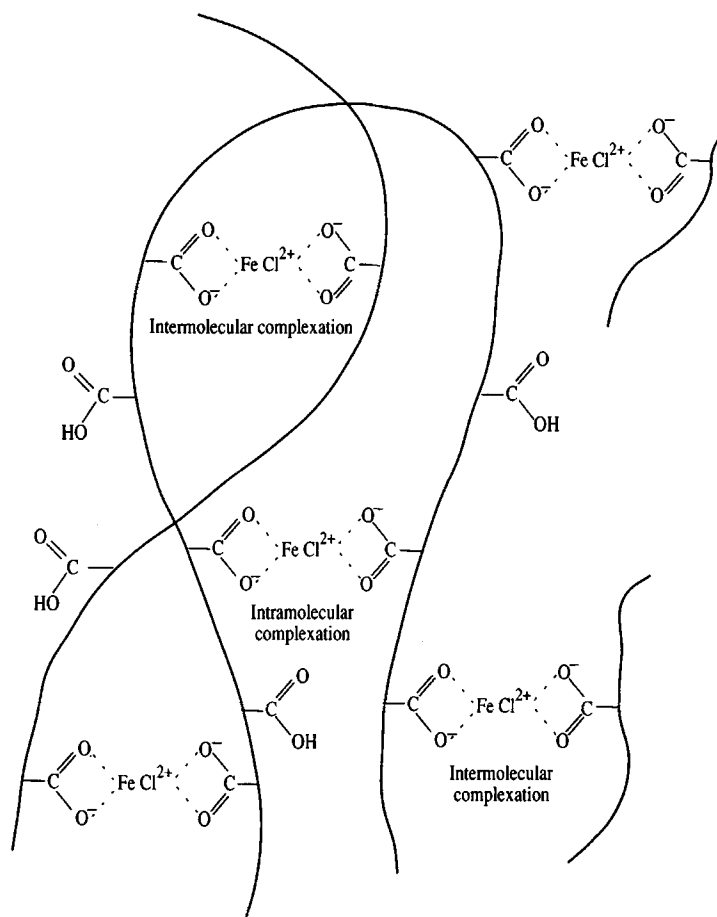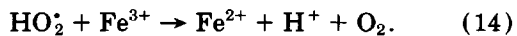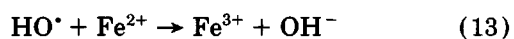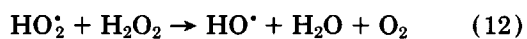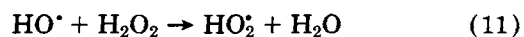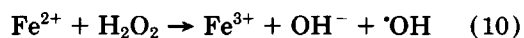
Figure 8 Probable mode of intramolecular and intermolecular complex formation between carboxyl groups and $FeCl^{2+}$ ions.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \qquad (10)$$

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad (11)$$

$$HO_2^\bullet + H_2O_2 \rightarrow HO^\bullet + H_2O + O_2 \qquad (12)$$

$$HO^\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (13)$$

$$HO_2^\bullet + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2. \qquad (14)$$

These chain-type reactions will occur until all H_2O_2 is decomposed into water and oxygen via formation of $HO^\bullet$ and $HO_2^\bullet$ radicals, and HO^- and H^+ ions:

$$HO^\bullet + HO_2^\bullet \rightarrow H_2O + O_2 \qquad (15)$$

$$HO^- + H^+ \rightarrow H_2O. \qquad (16)$$
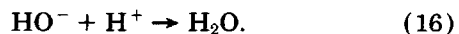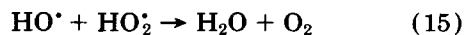
Reactions (10–14) explain why $FeCl_2$ does not give complexes with PAA in water, but easily in H_2O_2. The reason is that Fe^{2+} has to be oxidized to Fe^{3+} in order to form a complex with PAA. IR spectra

confirm that the structures of gels G-I, G-II, and G-III are almost identical. A similar conclusion can be drawn from the comparison of UV-vis spectra.

Both ferrous (Fe^{2+}) — H_2O_2[45-49] and ferric (Fe^{3+}) — H_2O_2[50] systems have been used to initiate graft copolymerization on cellulose,[45,46,49,50] wool,[48] and starch.[47] Hydroxyl $(HO^\bullet)$ and hydroperoxyl $(HO_2^\bullet)$ radicals formed in reactions (7), (9), (11), and (12) are involved in the abstraction of hydrogen from these polymers and the production of macro-radicals, which initiate grafting of added monomers. These results lead us to the assumption that both $HO^\bullet$ and $HO_2^\bullet$ radicals may also abstract hydrogen from the tertiary carbon in PAA molecules and form polymer radicals $(P^\bullet)$, which can give covalent crosslinks by the typical termination reaction:
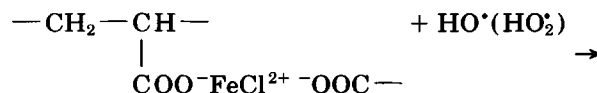
$$-CH_2-CH- \qquad\qquad + HO^\bullet(HO_2^\bullet)$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\qquad \rightarrow$$
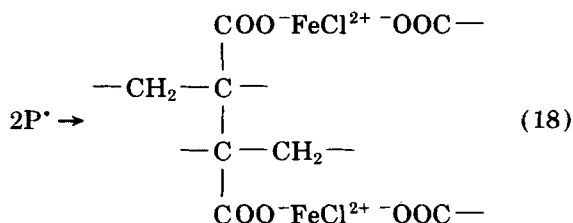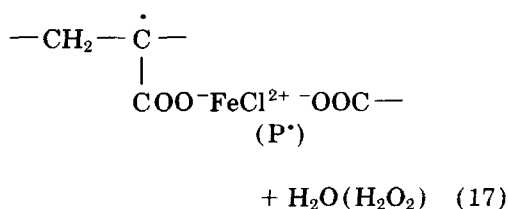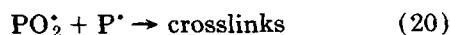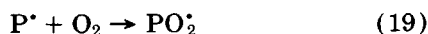$$COO^-FeCl^{2+}\ {}^-OOC-$$

Figure 9 (a)   SEM photomicrograph of a tooth channel blocked by the poly(acrylic acid)–FeCl$_3$ (2 : 1) gel (G-IC). Scale bar 1 μm (photograph by E. Adamczak and J. F. Rabek).

Figure 9 (b)   SEM photomicrograph of the channel entrance blocked by the poly(acrylic acid)–FeCl$_3$ (2 : 1) gel (G-IC). Scale bar 1 μm (photograph by E. Adamczak and J. F. Rabek).

$$-CH_2-\overset{\bullet}{C}-$$
$$|$$
$$COO^-FeCl^{2+} \ ^-OOC-$$
$$(P^{\bullet})$$

$$+ H_2O(H_2O_2) \quad (17)$$

$$COO^-FeCl^{2+} \ ^-OOC-$$
$$|$$
$$-CH_2-C-$$
$$2P^{\bullet} \rightarrow \qquad | \qquad\qquad (18)$$
$$-C-CH_2-$$
$$|$$
$$COO^-FeCl^{2+} \ ^-OOC-$$

Polymer alkyl radicals ($P^{\bullet}$) can be rapidly oxidized by oxygen formed in the *statu nascendi* reactions (9), (12), (14), and (15) to polymer peroxy radicals ($POO^{\bullet}$), which can also give peroxide crosslinking or form hydroperoxide groups:

$$P^{\bullet} + O_2 \rightarrow PO_2^{\bullet} \qquad\qquad (19)$$

$$PO_2^{\bullet} + P^{\bullet} \rightarrow crosslinks \qquad (20)$$

$$PO_2^{\bullet} + PO_2^{\bullet} \rightarrow crosslinks \qquad (21)$$

$$PO_2^{\bullet} + PH \rightarrow POOH + P^{\bullet} \qquad (22)$$

The decomposition of gels G-I, G-II, and G-III by concentrated HCl show that covalent crosslinking does not occur in the solutions of PAA–Fe salts in H_2O_2.

The $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals may also participate in the termination reactions with macroradicals ($P^{\bullet}$):

$$P^{\bullet} + HO^{\bullet} \rightarrow POH \qquad\qquad (23)$$

$$P^{\bullet} + HO_2^{\bullet} \rightarrow POOH. \qquad\qquad (24)$$

Hydroxy and hydroperoxy groups have strong IR absorption at $3451 \ cm^{-1}$ and may be overlapped with the strong band at $2882 \ cm^{-1}$ that belongs to the free stretching vibrations of OH in carboxylic groups. For that reason it is difficult to interpret the broad IR band in the $3500–2800 \ cm^{-1}$ region.

It has also been reported in the literature that hydroxyl radicals ($HO^{\bullet}$), formed in reaction (10), attack polyacrylamide in the solution and cause a chain scission.[51,52] We did not observe this reaction in the solutions of PAA–Fe salts in H_2O_2.

Complexation of polymers has considerable interest in polymer science because of potential applications in industry and medicine.[53,54] The PAA-$FeCl_3$ complexes have considerable dental significance. Both $FeCl_3$ and PAA dissolved in water easily
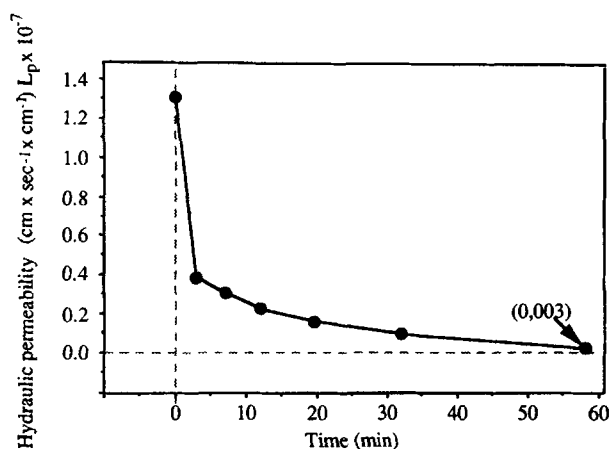

Figure 10 Kinetic curve of the hydraulic permeability of water through channels in the dentin blocked with poly(acrylic acid)–$FeCl_3$ (2 : 1) gel (G-IC).

diffuse into the biohydrogel that fills the dental tubules. After reaction with each other, a gel with a spongy structure is formed, which tightly blocks the channels [Fig. 9(a)] and the entrances of the dental tubules [Fig. 9(b)]. Blocking of channels has a tremendous effect on the flow of water through dentin (Fig. 10). The rapid decrease in the hydraulic permeability after $FeCl_3$ and PAA treatment of dentin during the first 10 min was followed by a slower decrease for the next 60 min (Fig. 10). This is probably due to delayed gelation that depends on the diffusion of both $FeCl_3$ and PAA through microscopic channels and also depends on the compression of formed gel in narrow parts of the tubules due to fluid flow pressure. Our development may have practical implications on dentinal hypersensitivity and caries.

CONCLUSIONS

On the basis of results obtained, we can conclude that the gels formed during the reaction between PAA and $FeCl_3$ in water or H_2O_2 and PAA and $FeCl_2$ in H_2O_2 have the same structure. Two carboxylic groups are involved in the complex formation with $FeCl^{2+}$ ions. Gels are crosslinked only by ionic bonds, not by covalent bonds. The gel formed from PAA–$FeCl_3$ in water has the ability to tighten channels in the dentin of human teeth and causes the decrease of fluid transportation through it. This is the first report in the literature on the possibility of the blocking of channels in teeth by employing polymer-metal salt complexes.

REFERENCES

1. M. G. Voronkov, A. T. Platonova, V. Z. Annenkova, et al. *Fr. Demande* **2,** 426,469, *Chemical Abstracts,* **92,** 22704x (1979), and *Jpn. Kokai Tokyo Koku,* **79,** 132240, *Chemical Abstracts,* **92,** 18513r (1979).
2. D. B. Poblinkov, V. M. Annenkova, N. G. Dianova, V. Z. Annenkova, and M. G. Voronkov, *Zh. Strukt. Khim.,* **30,** 149, *Chemical Abstracts,* **112,** 21504p (1989).
3. E. L. Zhdanovich, O. A. Trifonova, V. Z. Annenkova, and M. G. Voronkov, *Khim-farm.Zh.,* **23,** 883 *Chemical Abstracts,* **112,** 78287z (1989).
4. J. B. Lum and R. F. Beyer, U.S. Pat. 3,790,610 (1974); *Chemical Abstracts,* **81,** 26856f (1974).
5. H. Yokoi and N. Nishi, *Chem. Lett.,* 1765 (1989).
6. V. Z. Annenkova, A. T. Platonova, G. M. Konanchuk, et al. *Khim-Farm.Zh.,* **16,** 322, *Chemical Abstracts,* **96,** 193159x (1982).
7. V. Z. Annenkova, V. B. Kazmirovskaya, E. L. Zhdankovich, T. I. Nikiforova, O. A. Trifonova, and M. G. Voronkov, *Khim-Farm.Zh.,* **24,** 34, *Chemical Abstracts,* **113,** 129248t (1990).
8. L. L. Shisov, A. D. Katamakhin, and D. A. Topchiev, USSR Pat. SU 1,386,136 (1988); *Chemical Abstracts,* **109,** 37227z (1988).
9. V. N. Golubev, E. Zh. Ikukiradze, Z. D. Gusar, et al. USSR Pat. SU 1,375,221 (1988); *Chemical Abstracts,* **109,** 36902d (1988).
10. A. D. Wilson and J. W. McLean, *Glass-Inomer Cements,* Quintessence Publishing Co, Inc., Chicago, 1988.
11. L. Å. Lindén and Ö. Källskog, *Swedish Dental J.,* **16,** 56 (1992).
12. R. Ludewig, *Dent. zahnärzt,* **15,** 446 (1960).
13. W. Schöniger, *Microchem. Acta,* 123 (1956).
14. K. Abe, M. Koida, and E. Tsuchida, *Macromolecules,* **10,** 1259 (1977).
15. W. M. Anspanach and J. A. Marinsky, *J. Phys. Chem.,* **79,** 433 (1975).
16. J. A. Marinsky and W. M. Anspanach, *J. Phys. Chem.,* **79,** 439 (1975).
17. J. A. Marinsky, *J. Phys. Chem.,* **86,** 3318 (1982).
18. M. Morcellet, *Polym. Bull.,* **12,** 127 (1984).
19. R. Subramanian and P. Natarajan, *J. Polym. Sci., Chem. Ed.,* **22,** 437 (1984).
20. S. K. Chatterjee, N. Chatterjee, M. A. Khan, and S. Gosh, *Polym. Commun.,* **32,** 220 (1991).
21. L. J. T. Hughes and D. B. Fordyce, *J. Polym. Sci.,* **22,** 509 (1956).
22. A. Eisenberg, T. Yokoyama, and E. Sambalido, *J. Polym. Sci., Chem. Ed.,* **7,** 1717 (1969).
23. L. J. Bellamy, *The Infra-Red Spectroscopy of Complex Molecules,* Wiley, New York, 1954.
24. P. Monjol and C. Champetier, *Bull. Soc. Chim. Fr.,* **4,** 1302 (1972).
25. P. Monjol, *C. R. Acad. Sci. Ser. C,* **267,** 1021 (1968).

26. J. J. Mauer, D. J. Eustance, and C. T. Ratcliffe, *Macromolecules,* **20,** 196 (1987).
27. W. R. Feairheller, Jr. and J. E. Katon, *Spectrochim. Acta,* **23A,** 2225 (1967).
28. L. Bardet, G. Cassanas-Fabre, and M. Alain, *J. Mol. Struct.,* **24,** 153 (1975).
29. R. A. Frey, R. D. Werder, and H. H. Günthard, *J. Mol. Spectr.,* **35,** 260 (1970).
30. K. Nakamoto, *Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds,* Wiley, New York, 1986.
31. B. A. Gamlen and D. O. Jordan, *J. Chem. Soc.,* 1435 (1953).
32. E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.,* **64,** 335 (1942).
33. T. H. Siddal and W. C. Vosburg, *J. Am. Chem. Soc.,* **73,** 4270 (1951).
34. H. H. Bruun and S. Friberg, *Tappi,* **51,** 482 (1968).
35. H. Müller, S. Friberg, and H. H. Bruun, *Acta Chem. Scand.,* **23,** 515 (1969).
36. H. Müller, S. Friberg, and M. Hellsten, *J. Coll. Interface Sci.,* **32,** 132 (1970).
37. A. Katchalsky and H. Eisenberg, *J. Polym. Sci.,* **6,** 145 (1951).
38. T. S. Chen and J. K. Thomas, *J. Polym. Sci., Chem. Ed.,* **17,** 1103 (1979).
39. M. L. Brenerman, E. Yu. Gromova, A. Ye Usachev, G. Ya. Vasileva, and V. O. Barabanov, *Vysokomol. Soedin.,* **30A,** 1575 (1988).
40. V. B. Barabanov, G. Ya Vasileva, C. M. Yaroshevsky, and E. Yu. Gromova, *Vysokomol. Soedin.,* **25A,** 99 (1983).
41. J. F. Rabek, J. Lucki, B. J. Qu, and W. F. Shi., *Macromolecules,* **24,** 836 (1991).
42. F. Haber and J. Weiss, *Proc. Roy. Soc. London,* **147,** 332 (1936).
43. J. A. Christiansen, *Acta Chem. Scand.,* **9,** 272 (1955).
44. J. Koefoed, *Acta Chem. Scand.,* **9,** 283 (1955).
45. G. N. Richard, *J. Appl. Polym. Sci.,* **5,** 539 (1961).
46. C. E. Brockway and K. B. Moser, *J. Polym. Sci., Chem. Ed.,* **1,** 1025 (1963).
47. R. C. Burg, G. F. Fanta, C. R. Russell, and C. E. Rist, *J. Macromol. Sci. Chem.,* **2,** 93 (1968).
48. B. N. Misra, P. S. Chandel, and R. Dogra, *J. Polym. Sci., Chem. Ed.,* **16,** 1801 (1978).
49. B. N. Misra, R. Dogra, I. Kaur, and J. K. Jassel, *J. Polym. Sci., Chem. Ed.,* **17,** 1861 (1979).
50. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Appl. Polym. Sci.,* **12,** 2575 (1968).
51. D. K. Ramsden and K. McKay, *Polym. Degrad. Stabil.,* **14,** 217 (1986).
52. D. K. Ramsden and K. McKay, *Polym. Degrad. Stabil.,* **15,** 15 (1986).
53. E. A. Bekturov and L. A. Bimendina, *Adv. Polym. Sci.,* **45,** 99 (1981).
54. E. Tsuchida and K. Abe, *Adv. Polym. Sci.,* **45,** 1 (1981).