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Xin Qu[a]; A. Wrzyszczynski[b]; K. Pielichowski[c]; J. Pielichowski[c]; E. Adamczak[d]; S. Morge[d]; L. Å. Lindén[d]; J. F. Rabek[d]
[a] Department of Materials, Science and Engineering University of Science and Technology, Hefei, Anhui, People's Republic of China [b] Department of Chemistry, Technical and Agriculture University Seminaryjna 3, Bydgoszcz, Poland [c] Institute of Organic Chemistry and Technology Technical University Warszawska 3, Krakow, Poland [d] Polymer Research Group Department of Dental Biomaterials Karolinska, Institute (Royal Academy of Medicine), Huddinge (Stockholm), Sweden

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POLYMERIZATION OF CHITOSAN–ACRYLIC SALT FOR USE IN DENTISTRY

XIN QU

Department of Materials Science and Engineering
University of Science and Technology
Hefei, Anhui, People's Republic of China

A. WRZYSZCZYNSKI

Department of Chemistry
Technical and Agriculture University
Seminaryjna 3, Bydgoszcz, Poland

K. PIELICHOWSKI and J. PIELICHOWSKI

Institute of Organic Chemistry and Technology
Technical University
Warszawska 3, Krakow, Poland

E. ADAMCZAK, S. MORGE, L. Å. LINDÉN,*
and J. F. RABEK

Polymer Research Group
Department of Dental Biomaterials
Karolinska Institute (Royal Academy of Medicine)
Box 4064, S14104 Huddinge (Stockholm), Sweden

ABSTRACT

Polymerization of chitosan-acrylic acid salt ($CHI^{+-}AA$) has been studied in the presence of UV irradiation or by heat produced by Nd: YAG laser radiation. The polymer obtained photochemically, CHI-PAA, is soluble in water or saliva whereas the polymer obtained thermally, poly-CHI-AA, is strongly crosslinked by amide links and is insoluble in both water and saliva. Thermal polymerization of $CHI^{+-}AA$ allows for its application in the blocking of microchannels in dentin. Crosslinked poly-CHI-AA is much more resistant to enzymatic lysozyme degradation than $CHI^{+-}AA$ or CHI.

INTRODUCTION

Chitosan [2-amino-2-deoxy-(1,4)-β-D-glycopyranan] (CHI) is a well-known biocompatible natural polymer [1]. It has found a wide range of applications in medicine and dentistry. The CHI improved biocompatibility, cell migration, and inhibited adsorption of oral streptococci [2] prevents caries due to pH buffering and bacteriostatic actions [3]. Gel-forming, modified chitosans are more suitable for medical and dental use than CHI itself [4, 5].

It was reported in literature that a number of vinyl monomers such as acrylate [6], acrylamide [6] and acrylonitrile [6,7] can react with the amine and/or hydroxyl groups of CHI according to the reactions:

$$CHI{-}NH_2 + CH_2{=}CH{-}R \rightarrow CHI{-}NH{-}CH_2{-}CH_2{-}R \quad (1)$$

$$CHI{-}OH + CH_2{=}CH{-}R \rightarrow CHI{-}O{-}CH_2{-}CH_2{-}R \quad (2)$$

Consumption of unsaturated groups in these reactions does not allow their polymerization.

Acrylic acid (AA) reacts with CHI in the same way as many other acids, such as acetic acid [5, 8–10] formic acid [8], lactic acid [8], citric acid [11], and amino acids [12], giving the salt ($CHI^{+-}AA$):

$$CHI{-}NH_2 + HOOC{-}CH{=}CH_2 \rightarrow CHI{-}NH_3{}^{+-}OOC{-}CH{=}CH_2 \quad (3)$$

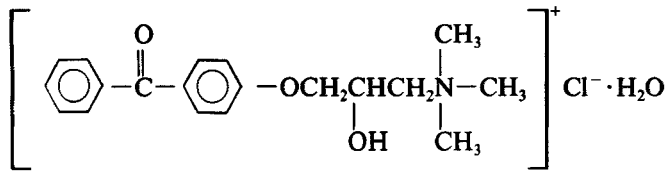
The presence of unsaturated groups in the $CHI^{+-}AA$ salt allows it to carry out the polymerization reaction with itself.

CHI and poly(acrylic acid) (PAA) form a salt ($CHI^{+-}PAA$) which highly swells in water to give a hydrogel. This hydrogel is used in the blocking of microchannels in human teeth [13]. However, the serious disadvantage of the $CHI^{+-}PAA$ gel is its susceptibility toward hydrolytic and enzymatic degradation in the presence of lysozyme, which limits its practical application in the oral environment. In order to overcome these difficulties, this paper presents our study on the preparation and polymerization of the chitosan-acrylic acid salt ($CHI^{+-}AA$). The laser-induced thermal polymerization of $CHI^{+-}AA$ gives an insoluble ladder-type polymer which can be used in the blocking of microscopic channels in tooth dentin.

EXPERIMENTAL

Chitosan (CHI) of low molecular weight, 70,000 (Fluka, Switzerland), and acrylic acid (AA) (Aldrich, Germany) were used to obtain the chitosan–acrylic acid salt ($CHI^+{}^-AA$) according to the following procedure: First, 5 g CHI was suspensed in distilled water (100 mL) at room temperature, then an access of AA (50 mL) was added dropwise to the stirred CHI suspension. After 2 hours the reaction between CHI and AA was stopped by the addition of a large amount of acetone (100 mL) which caused the precipitation of $CHI^+{}^-AA$. The reaction product was decanted in fresh acetone and dried at room temperature. The $CHI^+{}^-AA$ is partially soluble in water (up to 3 wt%). Films of $CHI^+{}^-AA$ (0.05 mm) were prepared by casting a 2 wt% solution on a glass plate and drying in air.

Photopolymerization was carried out in air in the presence of 3 wt% of a water-soluble photoinitiator, 2-hydroxy-3-(4-benzoyl-phenoxy)-*N,N,N*-trimethyl-1-propanaminium chloride monohydrate (Quantacure BPQ from Ward Blakinshop Ltd., UK):



using a high-pressure mercury lamp (Type HPK 125 W, Philips, Holland) (40 $W \cdot m^{-2}$) at a distance 20 cm and at room temperature.

Thermal polymerization was carried out in air without and/or with initiator (3 wt% of benzoyl peroxide, Aldrich, Germany) at 100°C in a drybox and/or at 60°C, respectively, using a dental Nd:YAG laser-35 (Laser Endotechnic, San Clemente, USA). The emitted radiation has a wavelength of 1064 nm in a pulsed mode (50 Hz) with an energy output variable from 3 to 25 W. The pulse length was 0.8 ms. Light was transmitted through fibers with 300 μm diameter, for which the energy density at 3 W was 1.8 $J \cdot mm^{-2}$. At 3 W the total energy delivered per 15 seconds was 45 J.

The IR absorption spectra were recorded with an FT-IR Perkin-Elmer 1650 spectrometer using sample films (0.05 mm) and by averaging 64 scans each time. The FT-IR kinetics of double-bond conversions were made with a Perkin-Elmer 842 IR spectrometer.

Molecular weight distribution curves were measured with a GPC Spectrophysics Model GP-8810 and a PL Aquagel Columns type 50. The eluent used was a mixture of 0.5 M acetic acid and 0.5 M sodium acetate.

DSC measurement was carried out with a Perkin-Elmer DSC-4 thermal analysis system at a standard heating and cooling rate of 10°C · min^{-1}. Samples of 3–4 mg were run in a nitrogen atmosphere over the 25–500°C temperature range. Indium (T_m = 156.6°C) was used for temperature calibration.

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

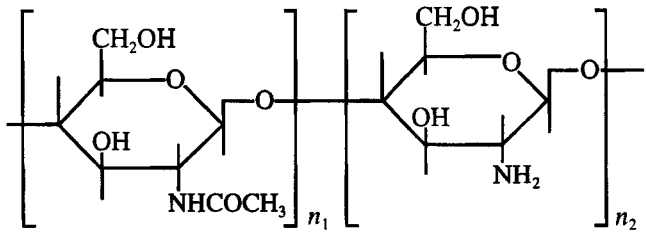
Scanning electron microscope (SEM) microphotographs were made with a Jeol JSM-820 scanning microscope.

Enzymatic degradation was carried out in a synthetic saliva of hen egg-white lysozyme (EC 3.21.17, 48,00 units·mg^{-1}, Sigma) according to the literature [14]. However, this procedure was changed a little: a sample of 500 mg $CHI^{+-}AA$ (or its product of polymerization), 50 μg lysozyme, and 1000 μg sodium azide in a solution of synthetic saliva, buffered to pH 5.4, was mechanically shaken at a temperature of 37°C. The absorbance at 415 nm of the reducing sugar produced was determined spectrophotometrically with a Beckman 7500 UV-vis spectrophotometer.

The synthetic saliva (similar to that of human saliva) consisted of 1.09 mM $CaCl_2$, 0.68 mM KH_2PO_4, 30 mM KCl, and 2.6 mM NaF. It was buffered to pH 7.0 with 50 mM *N*-2-hydroxyethylpiperazine-2-ethane sulfonic acid [15, 16].

RESULTS AND DISCUSSION

Chitosan (2-amino-2-deoxy-(1,4)-β-D-glycopyranan) (CHI) exists in different forms [1, 5]: as a random type or as a block type of copolymer of *N*-acetyl-D-glucosoamine units [17]:



Because of its pendant hydroxyl groups, CHI forms very strong intra- and intermolecular hydrogen bonds, making it infusible and insoluble in common solvents [1].

The degree of acetylated amine groups in our CHI sample was determined by IR to be 42.5% and the free amine groups to be 57.8% [13]. The broad amide IR band (Fig. 1) consists of two bands: a strong band at 1592 cm^{-1}, which is the result of coupling the amide vibrations with the neighboring amide groups in the crystalline or regular block regions, and a weak band at 1650 cm^{-1}, which can be attributed to uncoupled vibrations in the amorphous or less regular regions or in the vicinity of missing *N*-acetyl groups [18–21]. A complete interpretation of the IR spectra of CHI has been given elsewhere [19, 22, 23].

The chitosan-acrylic acid salt ($CHI^{+-}AA$) forms easily according to Reaction (3). SEM microphotographs show that its morphological surface structure (Fig. 2b) differs from that of CHI (Fig. 2a).

$CHI^{+-}AA$, even at low concentrations of 2 wt% in water or saliva, gives highly viscous solutions like honey. This drastic viscosity increase at such a small concentration of $CHI^{+-}AA$ can be attributed to interchain association through the formation of ionic microdomains (highly branched multichain aggregates) or the formation of a physical gel in which crosslinking is assured by ionic interchain aggregation. In artificial saliva, $CHI^{+-}AA$ solutions exhibit a more pronounced decrease in viscosity because the saliva salts screen the electrostatic repulsion be-

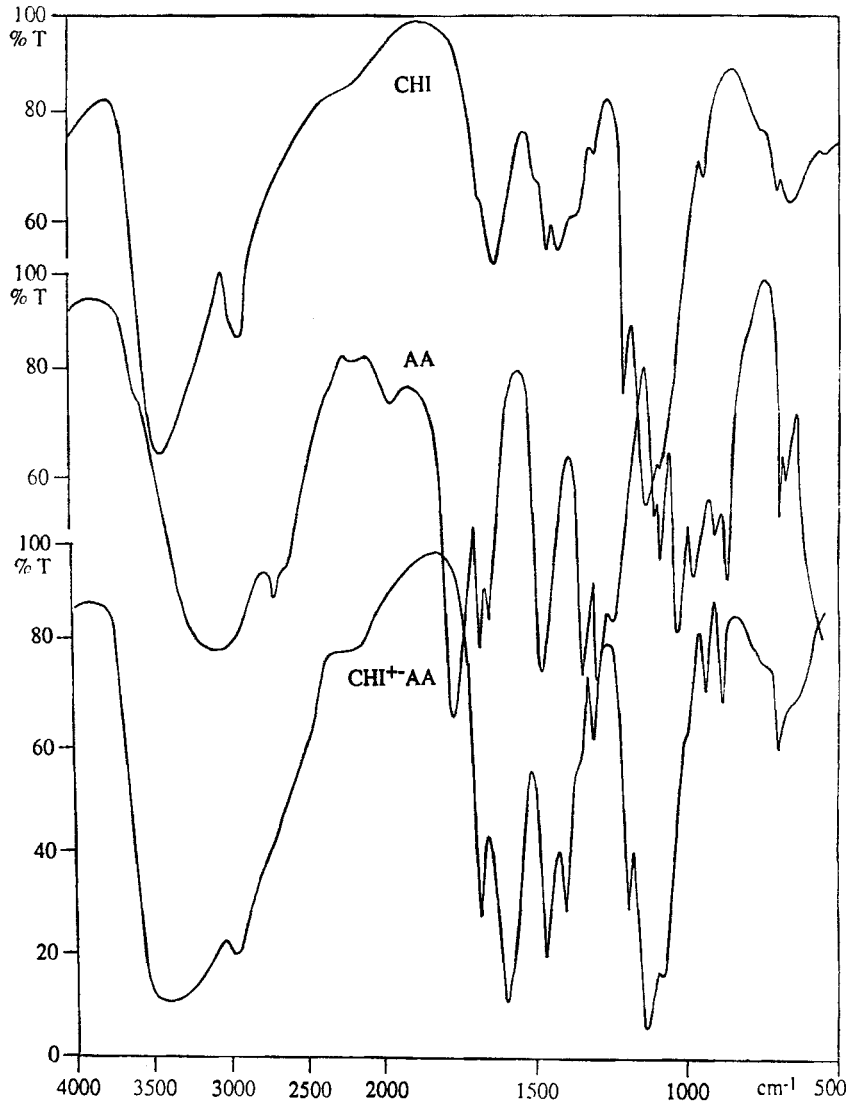


FIG. 1. IR spectra of CHI, AA, and $CHI^{+-}AA$.

tween charges along the $CHI^{+-}AA$ chains, which results in a more effective aggregation of polymer molecules. Addition of NaCl to associated $CHI^{+-}AA$ solutions leads either to a more pronounced decrease in viscosity or to a very effective thickening of the solutions.

At pH > 7, the actual charge density of the CHI-AA chain decreases, bringing about retraction of the chain and more effective ionic aggregation. Presumably, the addition of NaCl or a decrease in the pH does not have exactly the same influence on the association of ionic groups as on the polymer chain retraction.

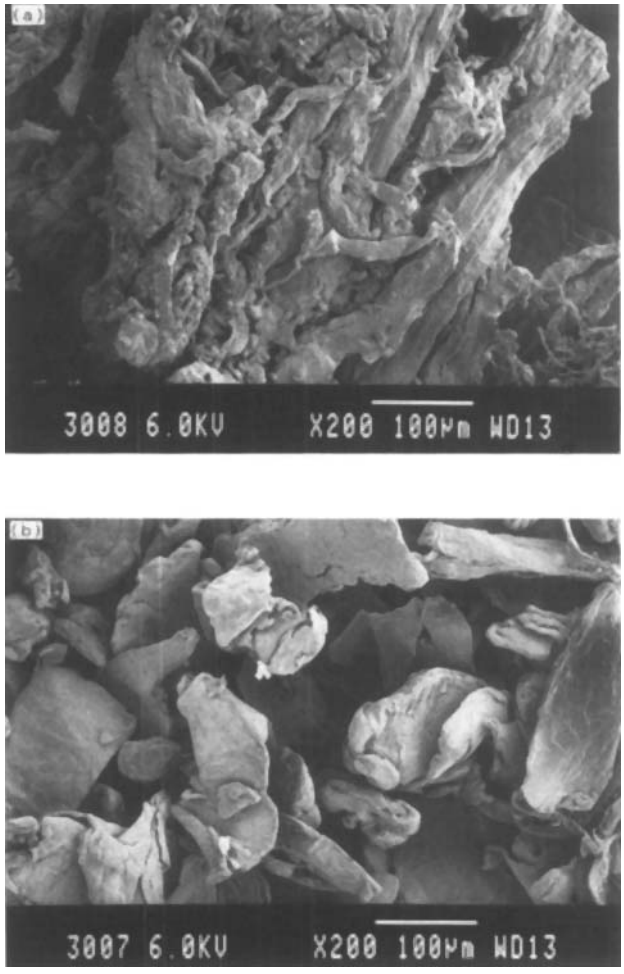
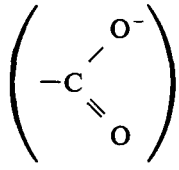
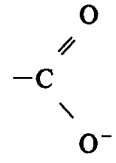


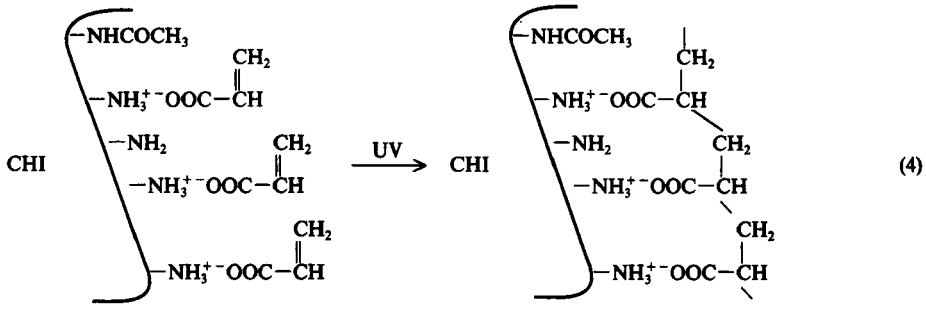
FIG. 2. SEM photomicrographs of (a) CHI and (b) $CHI^{+-}AA$.

The IR spectra of $CHI^{+-}AA$ (Fig. 1) shows characteristic bands for the presence of vinyl bonds ($CH=CH_2$) (in AA, Fig. 1) and the ionic form of the carboxyl group  (Table 1).

Photopolymerization of $CHI^{+-}AA$ in the presence of a hybrid photoinitiator system (based on camphorquinone and dimethyl-*p*-toluidine (1:1) at a concentration of 3 wt%, typical for photocuring of dental restorative materials [24–27]) and visible light (480 nm), does not occur. However, photopolymerization of $CHI^{+-}AA$ occurs in the presence of the water-soluble photoinitiator 2-hydroxy-3-(4-benzoylphenoxy)-*N,N,N*-trimethyl-1-propanaminium chloride monohydrate (Quantacure BPQ) (at a concentration of 3 wt%) and UV irradiation according to the reaction

TABLE 1. Characteristic IR Absorption Bands for AA and $CHI^{+-}AA$

AA (Fig. 1)	$CHI^{+-}AA$ (Fig. 1)	Assignments
820 cm^{-1}	836 cm^{-1}	C=C
1636 cm^{-1}	1636 cm^{-1}	C=C
1720 cm^{-1}	–	C=O vibrations of free carbonyl groups
–	1550 cm^{-1}	Ionic form of carboxyl group 



Conversion of double bonds in the photopolymerization of $CHI^{+-}AA$ is low and does not exceed 30% (Fig. 3). The kinetic rate of photopolymerization (R_p)

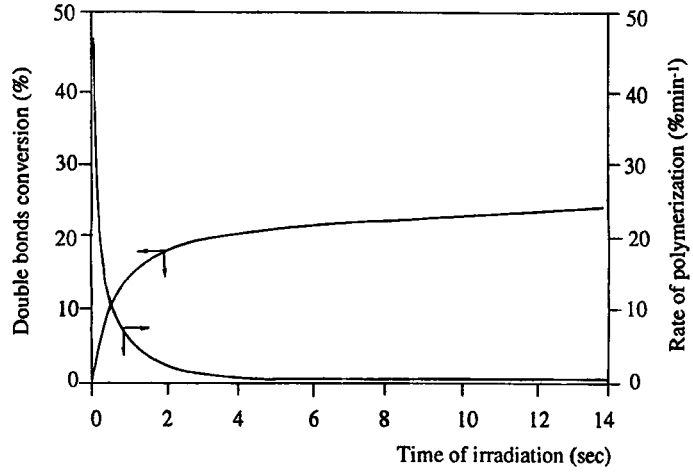


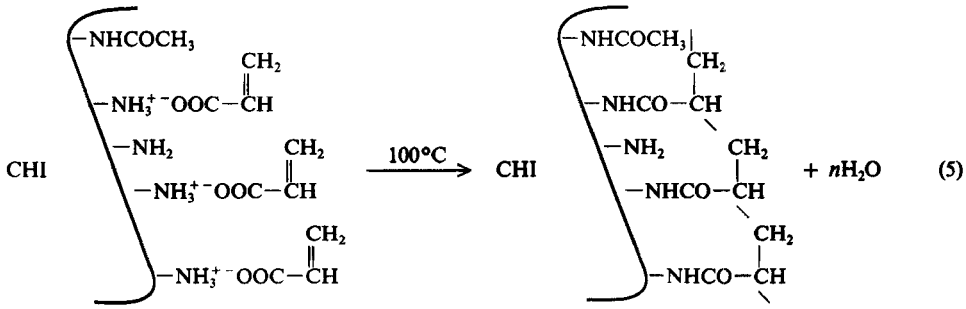
FIG. 3. Conversion of double bonds and rate of polymerization of $CHI^{+-}AA$ in the presence of 3 wt% Quantacure BPQ during UV irradiation.

shows that radical concentration rapidly increases immediately after switching on UV radiation for ca. 5 seconds and then decreases during the following 2 minutes (Fig. 3).

The polymer obtained from $CHI^{+-}AA$ (abbreviated $CHI^{+-}PAA$) in the form of a salt is readily soluble in water or artificial saliva. GPC measurements showed that the $CHI^{+-}PAA$ dissociates in water as a mixture of two polymers, CHI and PAA (Fig. 4).

The molecular weight distribution (MWD) of CHI molecules did not change during polymerization. The MWD curve of the PAA formed (Fig. 4, broken line) shows that the polymer has a low molecular weight and a broad MWD. This template polymerization of AA attached to CHI in salt form occurred only in regions where monomer molecules were distributed in random block sequences close enough to ensure the propagation reaction (Fig. 5). One can assume that the MWD of PAA gives some kind of mirrored image of the size and distribution of amine-group blocks in CHI. However, intra- and/or intermolecular chain propagation can lead to a completely wrong interpretation of the results.

Thermal polymerization of $CHI^{+-}AA$ occurs readily at 100°C with the evolution of water and, in addition, the formation of amide-type (—NH—CO—) links according to the reaction



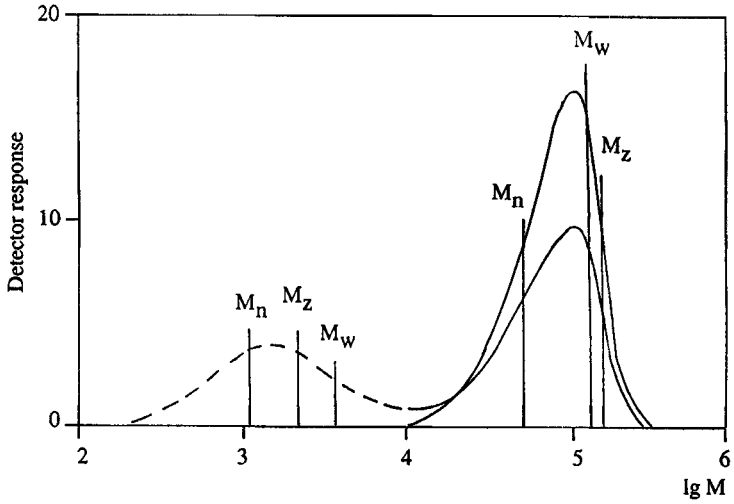


FIG. 4. Molecular weight distribution (MWD) of $CHI^{+-}AA$ and the product of its photopolymerization in the presence of 3 wt% Quantacure BPQ. The broken line represents the MWD of the PAA formed.

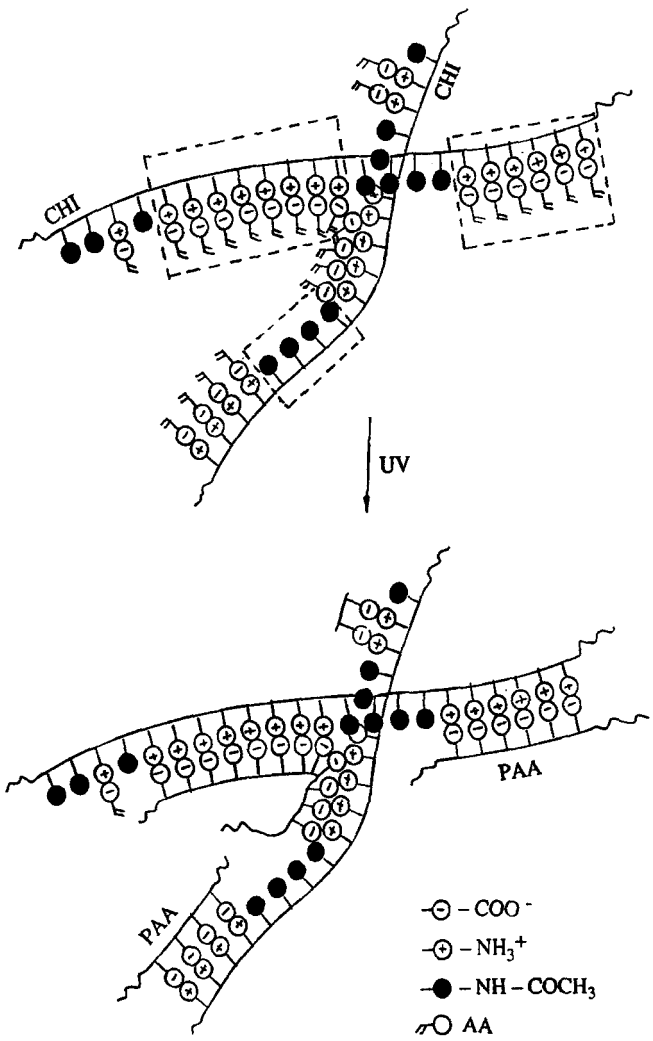


FIG. 5. Speculative representation of the photopolymerization of $CHI^{+}{}^{-}AA$ considering intra- and intermolecular chain propagation.

The formed polymer (abbreviated poly-CHI-AA) is no longer in the form of a salt. The IR spectrum of poly-CHI-AA (Fig. 6) shows the disappearance of the C=C bands at 1636 and 836 cm^{-1} (in the AA). Even a short heating of 10 minutes with 40% conversion of double bonds gives completely insoluble poly-CHI-AA in water (or saliva). After prolonged heating of a sample at 100°C for 2 hours, the conversion of double bonds increased to 75% (Fig. 7). The incomplete polymerization of double bonds in poly-CHI-AA can be explained by the formation of a very dense crosslinked structure which limits the propagation reaction to some extent.

The kinetic rate of thermal polymerization (R_p) shows that the radical concentration rapidly increases in the early stages (1 minute) of the reaction and then decreases during the following 15 minutes (Fig. 7).

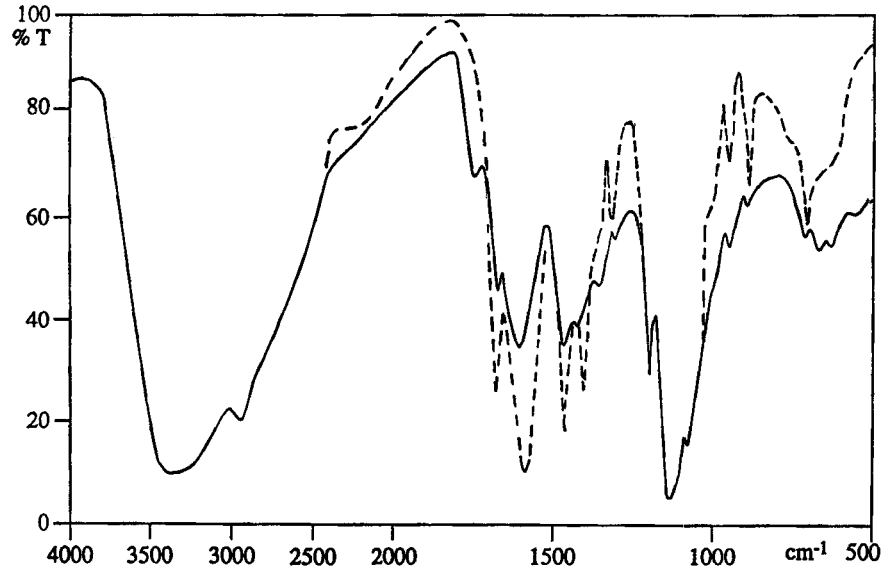


FIG. 6. IR spectra of $CHI^{+-}AA$ (broken line) and poly-CHI-AA (solid line).

Kinetic measurements of both thermal and photopolymerization of $CHI^{+-}AA$ indicates that in the very early stages of polymerization a dense network structure of polymers is formed by inter- and/or intrachain propagation. The rigid structure of the polymer matrix hinders the free approach of double bonds to the propagating radicals.

Poly-CHI-AA is strongly crosslinked and swells in water (or saliva) to produce a hydrogel. A SEM microphotograph of the gel dried by the liophylization proce-

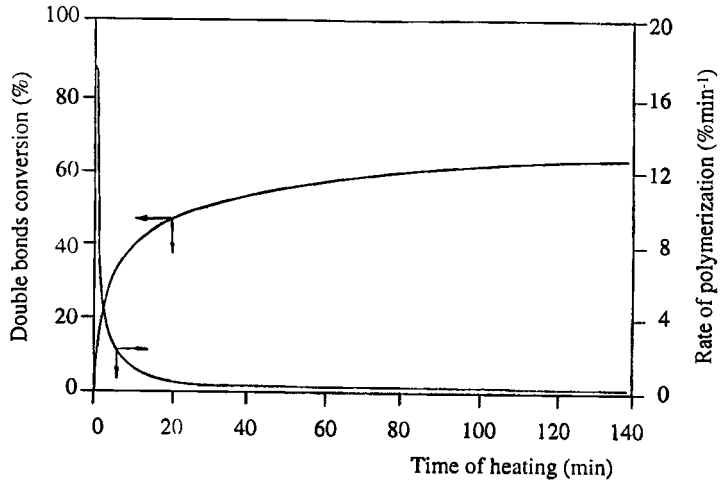


FIG. 7. Conversion of double bonds and rate of polymerization of $CHI^{+-}AA$ during thermal 100°C heating in a dry box.

dure shows the formation of big holes on the surface of the polymer film (Fig. 8).

All chemically modified CHI gels have a tendency to swell readily in various media, such as water, methanol, dimethylformamide, and dimethylsulfoxide, and they behave like anion-exchanging crosslinked polymers in aqueous solutions of acids and bases. The degree of swelling of poly-CHI-AA in water was 300% for the sample polymerized for 10 minutes at 100°C (with 40% conversion of double bonds); however, after prolonged heating at 100°C for 2 hours (with 75% conversion of double bonds), the degree of swelling decreased to 125%. The higher degree of swelling evidently depends on the presence of unreacted vinyl groups. In gels and solutions of polyelectrolytes, extracellular and intracellular matrices, and low and high density polymeric nets, swelling depends on the degree of crosslinking. The presence of unreacted vinyl groups between crosslinked macromolecules results in much more free space (available for water molecule penetration) than in a polymer networks in which all double bonds are polymerized.

The DSC thermogram of $CHI^{+-}AA$ shows the formation of one endothermic transition at 60–110°C (Fig. 9) which is the result of water elimination and the formation of amide links in Reaction (5).

The DSC thermogram of is in agreement with thermogravimetric analyses (TGA and DTG) of the $CHI^{+-}AA$ sample, showing that with increasing temperature the weight of sample decreases rapidly (15%) up to 110°C, slowly in the 110–180°C range, and then again very fast at higher temperatures due to thermal degradation of the poly-CHI-AA formed.

Differential thermal analysis (DTA) of $CHI^{+-}AA$ shows a large endotherm up to 110°C and two smaller endotherms during heating to higher temperatures (Fig. 10). The latter endotherms may be due to thermal decomposition of the poly-CHI-AA formed. These results indicate that during thermal polymerization of $CHI^{+-}AA$, water molecules are removed up to 115°C. During further heating of the poly-CHI-AA formed (Reaction 5) above 120°C, thermal oxidative degradation occurs; the sample turns brown at 150°C and black at 240°C. DTG measurements show that the maximum rate of decomposition of poly-CHI-AA occurs at 284°C,

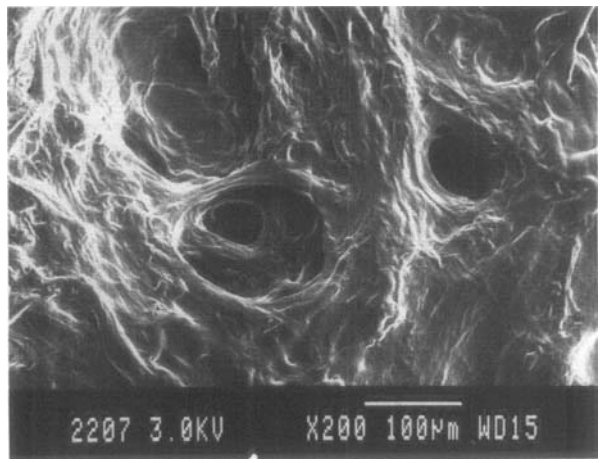


FIG. 8. SEM photomicrograph of poly-CHI-AA.

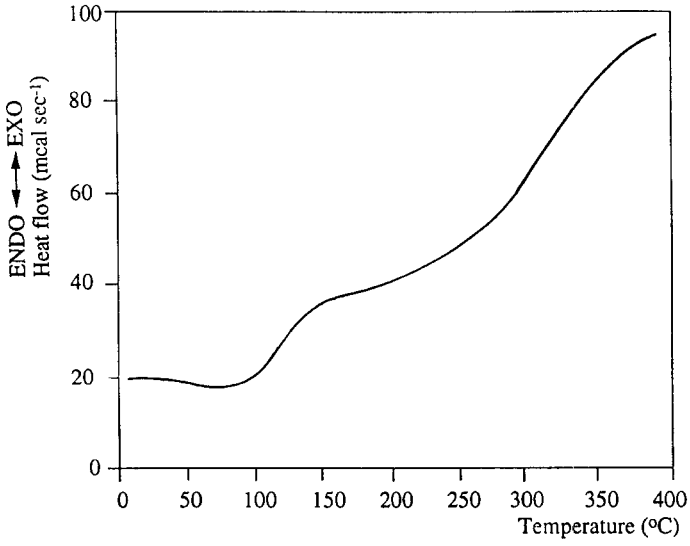


FIG. 9. DSC thermogram of $CHI^{+-}AA$.

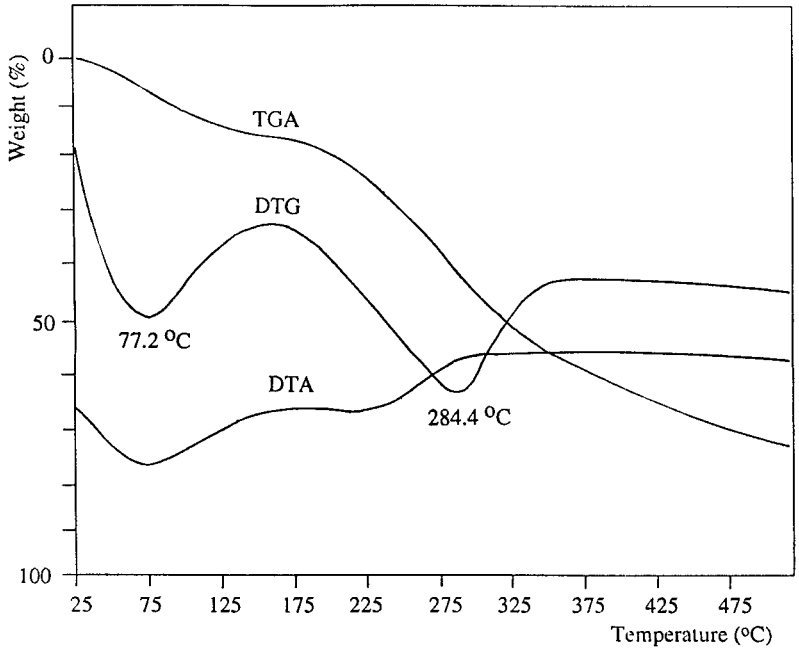


FIG. 10. Thermogravimetric curves (TG, DTG, and DTA) of $CHI^{+-}AA$.

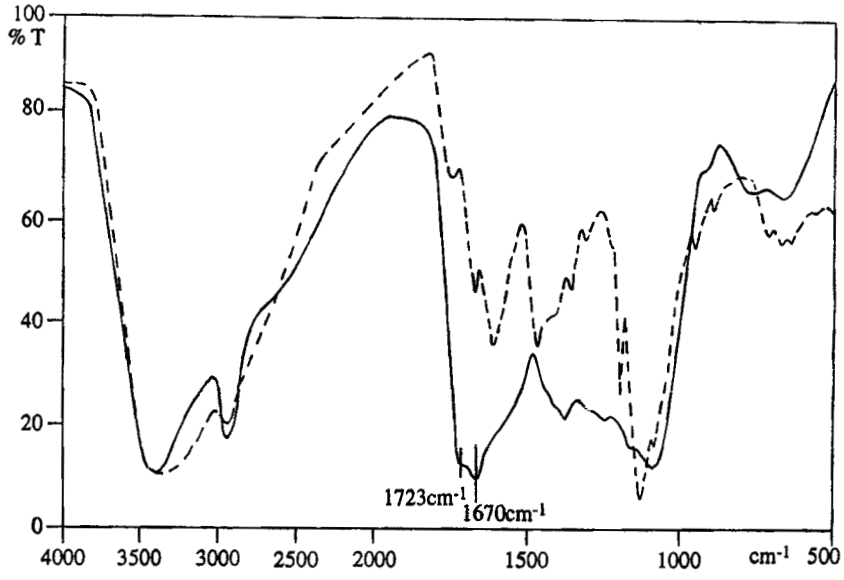
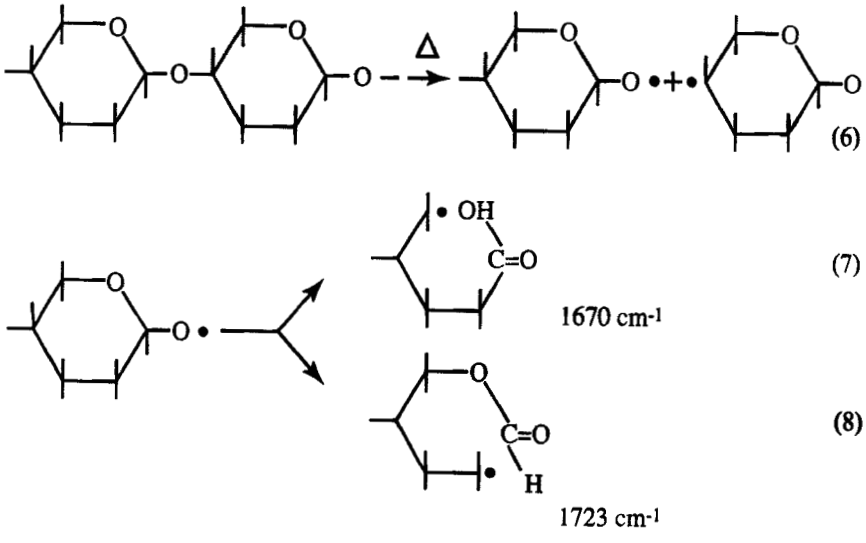


FIG. 11. IR spectra of poly-CHI-AA (--) and poly-CHI-AA thermally degraded at 220°C (—).

which is lower than the 303°C found for pure CHI. The presence of acrylate main chains in poly-CHI-AA may explain the decrease in its thermal stability.

The IR spectra of thermally oxidized poly-CHI-AA (Fig. 11) shows the formation of two very strong characteristic bands at 1723 cm^{-1} (carbonyl groups) and 1670 cm^{-1} (carboxylic group), which can be the result of thermooxidative cleavage of glucosidic bonds between the glucopyranose rings (Reaction 6) and ring-opening of the actual glucopyranose rings (Reactions 7 and 8):



For the practical use of $CHI^{+-}AA$ in dentistry, thermal polymerization can be carried out with heat produced by a dental laser. This method allows for direct polymerization in tooth channels or tooth cavities. However, irradiation of dental hard tissues with lasers leads to a variety of structural and ultrastructural tissue changes near the surface [28–31]. These changes depend on irradiation parameters such as wavelength, pulse duration, number of pulses, repetition rate, and beam spot size. The potential problems associated with the deposition of a large amount of energy in a tooth include thermal damage to the periphery of the treatment site, pulpal damage due to the transfer of excessive heat, charing of tissue, cracking of the enamel or dentin, and even melting of a material with the formation of holes (Figs. 12 and 13).

In order to avoid clinical problems, thermal polymerization of $CHI^{+-}AA$ has been carried out in the 60–80°C range in the presence of a thermal initiator, benzoyl peroxide (at a concentration of 3 wt%). A SEM photomicrograph of the dentin channels cross-section (Fig. 14) shows tight blocking with poly-CHI-AA. In addition, this microphotograph (at a magnification of 8000) shows the morphological structure of poly-CHI-AA much better than that shown in Fig. 8. A film of poly-CHI-AA produced on the dentin surface shows the formation of hundreds of small holes (Fig. 15) whose origin is difficult to explain. One hypothesis to be considered is that holes are formed directly above the entrances to the dentine channels in which successive polymerizations of $CHI^{+-}AA$ have occurred. However, the formation of such holes (but larger) was also observed in dried poly-CHI-AA hydrogel (Fig. 8).

The in vivo, laser-induced, thermal polymerization of $CHI^{+-}AA$ (in water or saliva solutions in teeth) is additionally complicated by the fact that dentin and water have different properties for absorbing and conducting heat [32]. Water requires nearly four times more energy than does dentin to raise the temperature to

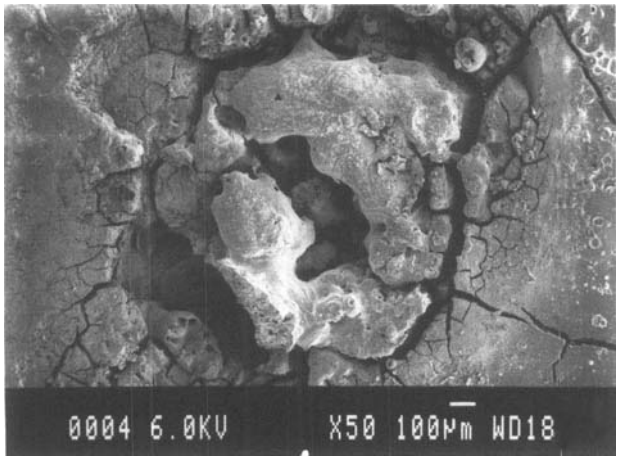


FIG. 12. SEM photomicrograph of damaged structure of human enamel due to heat emitted from Nd : YAG laser. Laser beam spot was localized in direct contact with tooth surface (~0.1 mm).

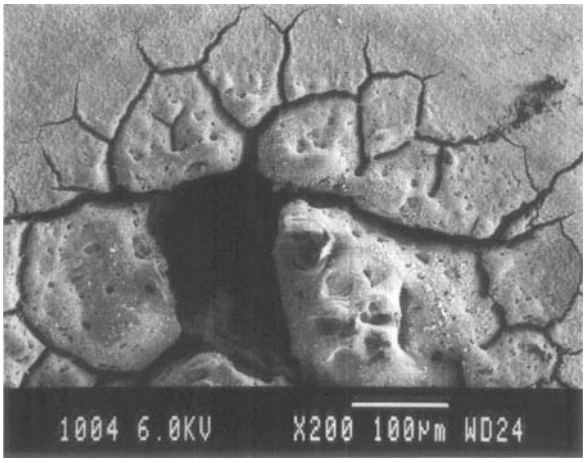


FIG. 13. SEM photomicrograph of damaged structure of human dentin covered with poly-CHI-AA by heat emitted from Nd : YAG laser. Laser beam spot was localized in direct contact with the sample surface (~0.1 mm).

the same degree [33]. Dentin and water conduct heat at about the same rate. Because the density of dentin is 2.1 compared to 1.0 for water, the thermal diffusivity is higher for dentin than for water. From this, it follows that dry and wet channels will absorb energy differently. This causes a problem of overheating dentin in an attempt to obtain high conversion of the double bonds in $CHI^{+}\,^{-}AA$. Dentists must

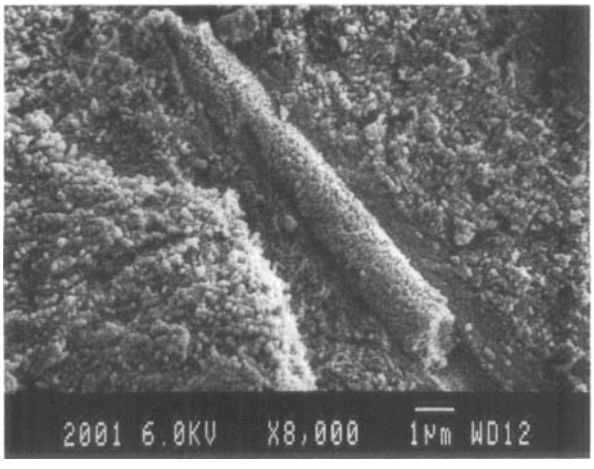


FIG. 14. SEM photomicrograph of the dentin channel blocked by poly-CHI-AA. Thermal polymerization was carried out in the presence of 3 wt% benzoyl peroxide at 60–80°C. The laser beam spot was localized ~20 mm from the sample surface.

take special care to adjust the laser energy to a level that prevents a hazard to dentin and the surrounding tissues.

Pure CHI is very hydrophilic and is therefore susceptible to hydrolysis [1, 5]. CHI membranes could be more or less effectively degraded depending on the pH and the degree of deacetylation, with optimal values at pH 5–6 and degree of deacetylation 0.66–0.80 [14, 34, 35]. Susceptibility of CHI toward enzymatic lysozyme degradation also depends strongly on the degree of deacetylation [14, 35]. The kinetics of enzymatic degradation of CHI and modified chitosans, which are soluble in acidic water solutions, can be followed by molecular weight determination using viscometric measurements [36] or spectrophotometrically [14]. The enzymatic degradation of CHI by hydrolysis is probably a two-step process in which the enzyme lysozyme first binds to the polymer substrate and then catalyzes hydrolytic cleavage. The initial attack on CHI occurs via endo attack at any location along the length of the polymer chain, resulting in a mixture of lower molecular weight products. The product of photopolymerization of $CHI^{+-}AA$, i.e., $CHI^{+-}PAA$, which is soluble in water (or saliva), is susceptible to enzymatic lysozyme degradation as is $CHI^{+-}AA$ (Fig. 16). The poly-CHI-AA obtained by thermal polymerization of $CHI^{+-}AA$ is swellable but insoluble in water. In this case the enzymatic lysozyme degradation is heterogeneous and confined to the surface of the sample, since lysozyme is unable to penetrate into the bulk of the substrate. However, the hydrolysis reaction products are water-soluble and can diffuse away from the bulk once generated. In this case, enzymatic lysozyme degradation occurs much less efficiently (Fig. 16).

The fact that poly-CHI-AA is less susceptible to enzymatic lysozyme degradation than CHI or $CHI^{+-}AA$ makes it more suitable for applications in dentistry.

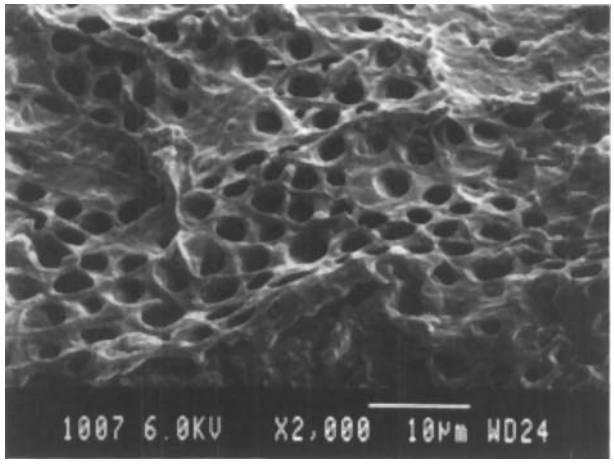


FIG. 15. SEM photomicrograph of the surface of dentin covered with poly-CHI-AA. Thermal polymerization was carried out in the presence of 3 wt% benzoyl peroxide at 60–80°C. The laser beam spot was localized ~20 mm from the sample surface.

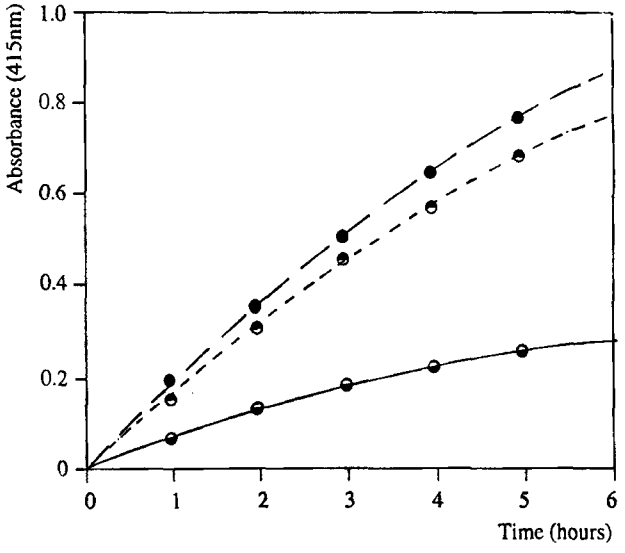


FIG. 16. Kinetics of enzymatic lysozyme hydrolyses of $CHI^{+-}AA$ (– –), $CHI^{+-}PAA$ (- - -), and poly-CHI-AA (——).

CONCLUSIONS

Chitosan–acrylic acid salt ($CHI^{+-}AA$) can be polymerized photochemically in the presence of photoinitiators, giving a water-soluble polymer, chitosan–poly(acrylic acid) salt ($CHI^{+-}PAA$). Thermal polymerization of $CHI^{+-}AA$ at 100°C in a dry box or at 60–80°C in the presence of a thermal initiator, benzoyl peroxide (using heat emitted by a Nd:YAG laser), gives a water-insoluble poly-CHI-AA. Thermally polymerized $CHI^{+-}AA$ can be used for blocking channels in dentin. Poly-CHI-AA is resistant to enzymatic lysozyme degradation.

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