Characterization of Acrylic Dental Polymers

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SUMMARY: The chemical structure and the molecular parameters of four dental acrylic polymer materials (samples P-1 to P-4) and two polyacrylic acids of different molecular weight (relative molecular mass) used as model compounds (samples Paa-1 and Paa-2) were studied and correlated with polymer structure and molecular weight. All polymer samples show low molecular weights, MW, and broad poly-dispersity as obtained by GPC. Samples P-3 and P-4 show the lower MW and bi-modal distribution, one peak corresponding to the polymer and the other to a low molecular weight compound at a lower concentration. The other polymer samples show unimodal distribution. Initially, all samples were soluble in water and dioxane above 99.8%. However, after lyophilization at -50 °C they showed different degrees of solubility because of partial gelation. The FTIR and, ^{1}H and ^{13}C-NMR spectra of Paa-1, Paa-2 in D_2O show the pattern characteristic of poly(acrylic acid). The polymers of P-1 and P-2 are mainly poly(acrylic acid). The P-3 spectra show the peak pattern for an (acrylic acid/methyl acrylate) copolymer of about 2:1 composition as calculated from the NMR spectra. The P-4 is an oligomer derived from 2-hydroxyethyl methacrylate. Solid ^{13}C-NMR spectra confirm the above structures and evidence anhydride formation after lyophilization. The MW and the linear expansion coefficient, α, were derived from *intrinsic viscosity in theta and perturbed conditions*. From this, the steric hindrance parameter, A, the molecular stiffness, σ, and the second virial coefficient, A_2, were calculated using different thermodynamic models. The Flory-Fox-Shafgagen and the Stockmayer-Fixman models fit better the experimental data and can be used to describe the molecular parameters of the acrylic polymers. Light scattering was used to compare results.

Introduction

Acrylic polymers find several applications in biomedicine. Soluble collagen/PAA water systems are used for the production of bio-artificial materials such as dialysis membranes, heart valves, artificial skin, hydrogels, etc. In dentistry, carboxylic acid based precursors polymerized by chemical promoters are widely used in restorations where photo-induced polymerization systems can not be applied. Most used precursors are based in low molecular weight polymers and copolymers of poly(acrylic acid) dissolved in water.[1]

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Polymeric materials employed in dentistry must meet several physical, chemical, biological and aesthetic requirements. Acrylic and methacrylic functional polymer systems are widely used because they approach many of these requirements. In addition, they must be prepared to meet proper viscosity and long shelf life in liquid state, in-site good mixing and handling properties, adequate working time, good strength and hydrolytic stability in the cements.[2] However, there are still problems to be solved related to the dimensional stability of the polymers during and after setting in combination with interfacial effects that require a more deep knowledge of the structure, size and shape of the polymer molecules involved.

It is well known that the mechanical and rheological properties of polymers can be estimated when the molecular weight (relative molecular mass) and molecular weight distribution are known along with a good understanding of polymer chain conformation. Because chain conformation depends on molecular weight, several conformations may be present in a polymer material.

Poly(electrolytes) show aggregation phenomena that have not been completely understood and Coulombian interactions can not be explained by simple superposition of electrolytes and polymer properties.[3,4]

Based on these considerations, the chemical composition, dimensions, and the molecular parameters of four acrylic polymers systems are analyzed by nuclear magnetic resonance and infrared spectroscopy, gel permeation chromatography, intrinsic viscosity and light scattering.

Theory

The viscosity-average molecular weight, M_v, can be estimated by using the Mark-Houwink equation:

$$[\eta] = \mathbf{K}(M_v)^a \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity, **K** and a are constants for a particular polymer-solvent pair at a particular temperature. The value of a in the Mark-Houwink equation is predicted to vary from 0.5 at theta-conditions to about 0.8 in a thermodynamically good solvent. More generally, a equals zero for hard spheres, about unity for semi-coils, and two for rigid rods.

The quantity **K** can be expressed in terms of the universal constant Φ:

$$\mathbf{K} = \Phi(\langle R_o^2 \rangle / Mv)^{3/2} \quad (2)$$

where $\langle R_o^2 \rangle$ represents the mean square end-to-end distance of the unperturbed coil.

The intrinsic viscosity of coiling polymers of moderate molecular dimensions follow the well known relationship:

$$[\eta] = \Phi \langle R^2 \rangle^{3/2} / M \quad (3)$$

where $\langle R^2 \rangle$ is the mean-square end-to-end distance of the perturbed coil and M is the molecular weight. When M_v is used, Φ equals to $2.2X10^{21}$ and when M_n is used, it equals to $2.5X10^{21}$ dL/(mol cm^3).

The expansion of the coil, α, in a thermodynamically good solvent is given by:

$$\alpha = \langle R^2 \rangle / \langle R_o^2 \rangle \quad (4)$$

The Mark-Houwink equation is often expressed in the following forms:

$$[\eta] = \Phi(\langle R^2{}_o \rangle^{3/2} / M)\alpha^3 = \mathbf{K} M^{1/2} \alpha^3 \quad (5)$$

In general, the quantity $R^2{}_o/M$ is roughly constant but the values of α_η increase with MW. In a good solvent the macromolecule has an extended conformation and [η] will be the highest.

A unique solution state arises in theta-conditions, that is when the second virial coefficient, $\mathbf{A}_2$ equals zero. [5] Under these conditions:

$$[\eta]_\theta = \mathbf{K}_\theta (M_v)^{1/2} \quad (6)$$

$\mathbf{K}_\theta$ is defined as follows:

$$\mathbf{K}_\theta = \Phi A^3 \quad (7)$$

$$A^2 = \langle R_o^2 \rangle / M \quad (8)$$

where the steric hindrance parameter, *A*, depends upon bond lengths, bond angles, and restrictions to rotation.

From equations (3) and (7):

$$[\eta]/[\eta]_\theta = \alpha_\eta^3 \tag{9}$$

In perturbed conditions the expansion of the coil in dilute solutions of linear flexible chains depends upon the excluded volume function, z: [6,7]

$$z = (3\pi/2)^{1/2} (B/A^3)M^{1/2} \tag{10}$$

where B is the polymer/solvent interaction parameter, which depends on the binary group integral, β, and molecular weight of the equivalent segment, M_s:

$$B = \beta/(M_s)^2 \tag{11}$$

The thermodynamic models used here to study the properties of polymers are described next. The Flory-Fox-Schaefgen's model (FFS) assumes that α_n can be expressed by the linear expansion factor in terms of the radius-of-gyration, α_s. From this, the following equation can be used:

$$[\eta^{2/3}]/M^{1/3} = K^{2/3} + 0.858\, K^{2/3}\Phi_o BM/[\eta] \tag{12}$$

This model fits well with experimental data near the theta-temperature. However, K yields negative values for high molecular weight fractions dissolved in good solvents.

The Stockmayer-Fixman's model (SF) assumes that α_n can be estimated from the linear expansion factor expressed in terms of the end-to-end distance , α_r. From this:

$$[\eta^2]/M^{1/2} = K + 0.51\Phi_o BM^{1/2} \tag{13}$$

where K is a constant. This model also fits well with experimental data, but for high molecular weights it deviates from the linear behavior.

Inagaki and Ptitsyn (IP) proposed a modified equation to correct deviations towards linear behavior:

$$[\eta^{4/5}]/M^{2/5} = 0.786K^{4/5} + 0.454K^{2/15}(\Phi_o)^{2/3}B^{2/3}M^{1/3} \tag{14}$$

However, this model works well only for high molecular weight polymers.

Berry's model (Be) seems to hold for a wide range of molecular weights except for low ones.

$$[\eta^{1/2}]/M^{1/4} = K^{1/2} + 0.42K^{1/2}\Phi_o BM/[\eta] \quad (15)$$

The parameter A can be estimated from the value of $A_2M^{1/2}$ at the zero limit of $<S_o^2>/M$, where $<S_o^2>$ is the mean-square radius-of-gyration,

$$1.42 \times 10^{24}A_2M^{1/2} = -A^3 + 6A<S^2>/M \quad (16)$$

Krigbaum (Kr) developed a semiempirical equation to estimate $\mathbf{A_2}$:

$$[\eta] = [\eta]_\theta + 0.005A_2M \quad (17)$$

The length of the statistic element b, $<R_o^2>$, $<S_o^2>$, and the stiffness coefficient, σ, can be estimated by using the following equations:

$$b = (K_\theta/\Phi)^{1/3}(m_o)^{1/2} \quad (18)$$

$$<R_o^2> = MA^2 \quad (19)$$

$$<S_o^2> = MA^2/6 \quad (20)$$

$$\sigma = (<R_o^2>/M)^{1/2}/(<R_{of}^2>/M)^{1/2} \quad (21)$$

where m_o is the molecular weight of the repeating unit and $<R_{of}^2>$ is the mean-square end-to-end distance for the freely rotating chain.

The molecular properties of poly(acrylic acid) solutions at perturbed and unperturbed conditions have been widely studied by intrinsic viscosity, light scattering, and other methods.[8] The properties of PAA fractions of molecular weight prepared by stepwise precipitation in a two phase system (1,4 dioxane/heptane), redissolution of dry fractions in 1,4-dioxane and filtration has also been carefully studied.[9] Series of fractions of PAA in anhydrous 1,4-dioxane, considered as a poor solvent for this polymer, at the theta-temperature (30 °C) fit with the above relationships. At these conditions **K** is equal to 8.5×10^{-4} dL/g.

The solutions of PAA in anhydrous 1,4-dioxane are of nonionic character. However, in non-anhydrous 1,4-dioxane (2 to 5% of water) hydrogen bonding increases as well as chain stiffness. In these conditions, **K** equals $6.6(\pm 0.2) \times 10^{-4}$.

In gel permeation chromatography, diffusion through a porous column depends upon the size of the molecule, which is defined by its hydrodynamic radius. The average molecular size is given by equation (3) that can be written as:

$$[\eta]M = \Phi\langle R_o^2\rangle^{3/2}\,\alpha^3 \qquad (22)$$

where the right-hand side is proportional to the polymer's hydrodynamic volume.[10,11]

The universal calibration method has been used here on the basis of equation (22) because separation in a GPC column depends upon the hydrodynamic volume rather than its molecular weight. The molecular weights reported are actually those of the equivalent radius-of-gyration of the used polystyrene standards (Mw/Mn<1.2). This method can be used for almost all linear atactic poly(acrylic) acid and its homolog, poly(methacrylic acid), in its non-ionized form.[8] The universal calibration procedure is specially useful for estimating the molecular weight of new polymers, since the intrinsic viscosity can generally be easily obtained.

The angular variation of the scattering intensity provides a measure of the molecular size. Scattering techniques yield *z*-average radius-of-gyration and weight average molecular weights, Mw. To correct the data for proper comparison the molecular weight needs to be known, or very sharp molecular weight standards need to be used.[12,13]

Both melt and solution viscosities depend directly on the radius-of-gyration, R_g, of the polymer and on the chain capability of being deformed. Values of $[R_g/Mw]^{1/2}$ are substantially the same in the bulk as in theta-solvents, this quantity is also a measure of chain stiffness. The importance of these quantities lies in their relationship to physical and mechanical behavior of the polymer.

For random coils obeying Gaussian statistics $\langle R^2\rangle$ depends upon both the molecular weight and a function of the chain molecular structure, C:

$$\langle R^2\rangle = CM \qquad (23)$$

Experimental

Materials

The two polyacrylic acids, used as model compounds, were prepared by free radical polymerization in aqueous solution using reagent grade (Aldrich) acrylic acid monomer,

ammonium persulfate as initiator, 2-propanol as chain transfer agent and deionized water. The polymerizations were carried out as described elsewhere, [14] in a 300 mL 316 stainless steel reactor (Parr Instruments Co.) equipped with a reflux column and, stirring and temperature automatic controls, in conditions to minimize the formation of ramifications and crosslinking.

The obtained polymers were purified by precipitation and redissolved in 1,4-dioxane. The solvent was eliminated by vacuum drying at 60 °C. The polymers consisted of about 88% polyacrylic acid as obtained by titration with NaOH standard solution.

The other systems were dental polymers and copolymers provided by the Schools of Dentistry (P-1 to P-4) and Chemistry (PS series) at UNAM. Other chemicals from Aldrich: 2-hydroxyethyl methacrylate, methyl acrylate, methacrylic acid, +(-) tartaric acid, itaconic acid, and maleic acid (model compounds) were used as received. The polymers P-1 to P-4 were selected by their good performance in dental materials. Their structure and properties are described below in Results and discussion section.

Procedures

NMR and FTIR. The chemical structure of the polymers, model compounds, and monomers was first studied by ^{1}H and ^{13}C NMR and FTIR spectroscopies. Solution NMR spectra were recorded on a Varian Gemini 200 and in a Varian Unity Plus 300 spectrometers. The solid-state NMR spectra were obtained under proton decoupling on a Varian Unity Plus 300 spectrometer operating at 75.74 MHz for ^{13}C. The CP-MAS spectra were typically recorded under Hartmann-Hann matching conditions with a contact time of 2 ms, a repetition time of 4s, and a spinning rate of 4.5 to 5 kHz. The measurements were made using a spin-lock power in radio frequency units of 60 kHz and 1028 transients per spectrum were typically recorded. Elimination of spinning sidebands was typically accomplished by the TOSS sequence. Chemical shifts were referenced to the right peak of adamantane at 29.5 ppm. Chemical shifts in D_2O and $CDCl_3$ (depending on the solubility of the material) were referenced to DSS or TMS respectively. Two dimension spectra were obtained by using the pulse sequences for HETCOR and COSY. The FTIR spectra of the monomers, model compounds and polymers, were obtained with a Nicolet 510P spectrophotometer. Solution and thin film solid state spectra of polymers were recorded on standard CsI substrates. The sample reference was air.

Solubility Tests. To study the effects of dehydration, rehydration and solubility the polymers were dried by lyophilization at -50 °C and 0.08 mbar, using a Hectosic Co. instrument equipped with a RZ2 rotatory vacuum pump. After measuring the solid content, the dried polymers were redissolved separately in deionized water and in HPLC grade 1,4-dioxane previously filtered.

GPC. The average-molecular weights and molecular weight distributions of all polymers were determined by using a Waters GPC-150/C unit with Millipore μ-Bondagel separation columns, covering the range from 500 to $2X10^6$ g/mol. Ten mono-disperse polystyrene standards, from 500 to 500,000 g/mol dissolved in chromatographic grade 1,4-dioxane, previously degassed and filtered, were used for universal calibration. All polymer solutions were filtered through 0.22 μm Cole Parmer PTFE filters.

Intrinsic viscosity. Viscosity measurements were made in 1,4-dioxane at 30 °C, and in O.1M and 1.5M NaBr water solutions at 25 and 15 °C respectively, in an Ubbelode No. 1C capillary viscometer and following the ASTM Procedure D2857-87.

d*n*/d*c*. Refractive index increments, d*n*/d*c*, of polymer solutions in 1,4-dioxane were obtained by using a Brice-Phoenix Bp-200-v differential refractometer. After obtaining d*n*/d*c* values at wavelengths of 546 nm and 436 nm, the d*n*/d*c* at 632.8 nm was obtained by extrapolation from the Cauchy expansion equation. Reliability was obtained by measuring the d*n*/d*c* of monodisperse polystyrene standards dissolved in HPLC toluene. The obtained d*n*/d*c* values differ in ±0.002 from the value reported in the literature.[15]

Light scattering. Measurements were carried out in a multiangle laser light scattering Wyatt Technology Co. Dawn-F instrument, equipped with a He-Ne linearly polarized light source, (λ = 632.8 nm) in the batch-mode. Absolute calibration was previously performed, as recommended in the standard procedure, by using mono-disperse polystyrene standards dissolved in HPLC grade toluene.[12] To assure for absolute calibration, a value of 0.275 for $[R_g/Mw]^{1/2}$ was used for the polystyrene standards. By using the d*n*/d*c* values, obtained as described above, the weight-average molecular weight, the second virial coefficient and the RMS radius of the acrylic polymers dissolved in 1,4-dioxane were determined by the Zimm plot method.

Results and discussion

Composition

The average molecular weights as obtained by GPC are shown in Table 1. The broad polydispersity observed in the model compounds (Paa-1 and Paa-2) is attributed to the chain transfer agent present in the polymerization reaction. In samples P-3 and P-4 the second peak correspond to tartaric acid and/or maleic acid added after polymerization, and probably to dimers and trimers.

Table 1. Average molecular weights, g/mol, and polydispersities by GPC.

SAMPLE	Mn	Mw	Mz	Mv	Mw/Mn
Paa-1	5,920	56,800	219,890	56,790	9.6
Paa-2	3,990	44,630	137,360	44,330	11.1
P-1	5,331	26,560	58,890	26,550	5.0
P-2	3,530	19,900	41,640	19,800	5.6
P-3:					
1st Peak	4,740	12,400	25,540	12,400	2.6
2nd Peak	31	430	910	430	14.0
P-4:					
1st peak	1,470	4,650	9,820	4,650	3.1
2nd Peak	45	210	360	210	4.8

The infrared and NMR spectra, in both solution and solid state, of poly(acrylic acid) model compounds, samples Paa-1, Paa-2, were obtained in order to characterize the structures of the dental polymers. Polymer P-1 is mainly poly(acrylic acid) with a small amount of itaconic acid. For polymer P-2 only poly(acrylic acid) is observed. Polymer P-3 is an (acrylic acid/methyl acrylate) copolymer of about 2:1 composition, as calculated from the integration areas in the ^{1}H and ^{13}C NMR spectra. To calculate the ratio by the ^{13}C spectrum, a pulse sequence with Nuclear Overhauser Enhancement (NOE) suppression was used. P-4 is an oligomer derived from the 2-hydroxyethyl methacrylate precursor (Fig. 1). With respect to a typical spectra of poly(acrylic acid), the P-1 ^{1}H NMR spectrum shows an extra peak at 2.32 ppm, attributed to a small amount of an acryilic precursor. Two small peaks, at 5.7 and 6.2, were observed in the P-2 spectrum, due to the presence of residual monomer (acrylic acid). The FTIR spectra of

Paa-1, Paa-2, P-1 and P-2 also show the typical patterns of poly(acrylic acid). Published FTIR and NMR spectra, by Aldrich, Nicolet library, and spectra of model compounds, were used as a guide to accomplish bands assignment.

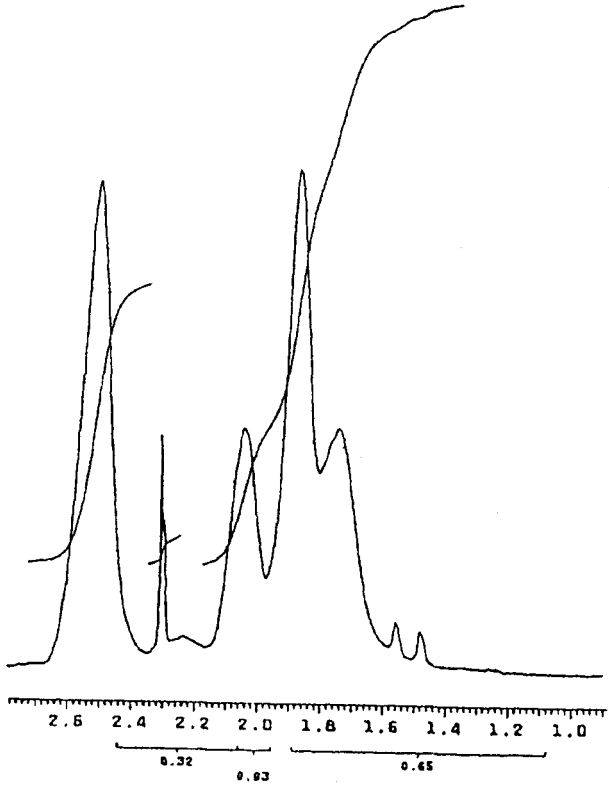

Figure 1. 300 MHz NMR spectrum of sample P-1 in D_2O (0.9 – 2.78 ppm region).

Initially, all samples were 100% water soluble. After lyophilization, the polymers showed different degrees of solubility. Water solubility of Paa-1 and Paa-2 was 99%, whereas for P-1 to P-4 was 98, 96, 89, and 81% respectively. The solubility in 1,4-dioxane changed from the initial 100% for each polymer to 96%, 96%, 91%, 95%, 59%, and 34% respectively. The crosslinked fraction is readily obtained by the difference from the solubility in water before and after lyophilization.

We found that lyophilization of acrylic acid polymers and (acrylic acid/methyl acrylate) copolymers favour intra and intermolecular anhydride formation. After redissolving the so dried samples in water and 1,4-dioxane gelation became apparent. Solid state ^{13}C-NMR spectra before and after lyophilization evidence the above-mentioned structures. The spectra of the polymers after lyophilization show a peak at 168-170 ppm, which corresponds to the carbonyl of a carboxylic anhydride. The ^{13}C-NMR spectrum of P-1 (Fig. 2) evidence the presence of intramolecular carboxylic anhydride cyclization in the redissolved fraction, probably involving adjacent repeating units, appears at 168.7 ppm.

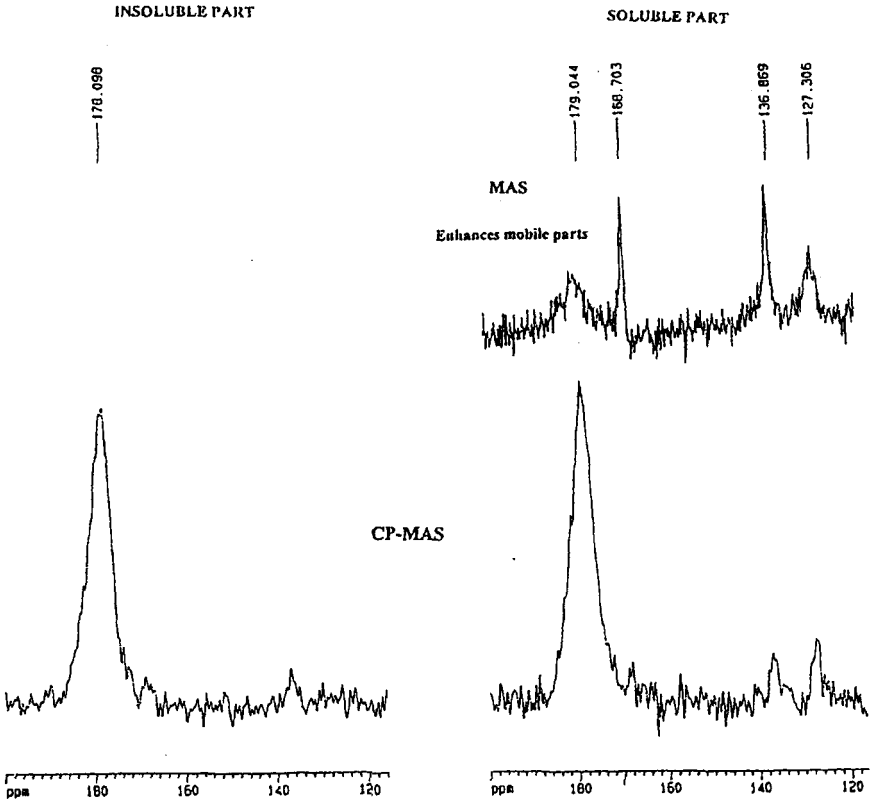

Figure 2. 2.75 MHz ^{13}C CP-MAS and MAS spectra of the insoluble and soluble fractions of sample P-1 after lyophilization.

Some authors have studied the behavior of poly(acrylic acid) and poly(methyl acrylate) after thermal treatment, all of them concluded that anhydride formation occurred on heating. The

main evidence for the loss of water is the appearance of a band in the infrared spectra at about 1750 cm^{-1} characteristic of carboxylic acid anhydrides, and a peak in the region of 169 to 172 ppm in the ^{13}C-NMR spectrum. Above 200 °C, intermolecular anhydride bridges are favoured, whereas at a lower temperature, 150 °C, intramolecular anhydride cyclization is favoured.[16,17]

The ^{1}H and ^{13}C NMR spectra of P-3 in D_2O (Fig. 3) evidence the structure of a copolymer (acrylic acid/methyl acrylate). In the HETCOR spectrum (Fig. 4) cross-peaks between carbons and protons present in the copolymer can be observed. The methoxy group appears at 4.6-4.7 ppm in the ^{1}H spectrum and 74.8 ppm in the ^{13}C spectrum. The ester and acid carbonyls appear at 177.5 and 181.7 ppm respectively. Lyophilization of this copolymer rendered an insoluble fraction of about 11%, suggesting anhydride crosslinking. It is very likely that an acrylic acid repeating unit adjacent to a methyl acrylate repeating unit form a cyclic carboxylic anhydride with the corresponding loss of methanol. The NMR spectra of the soluble and insoluble fractions of lyophilized P-3 were also recorded. The ^{13}C MAS spectrum of the soluble fraction (Fig. 5) evidence the presence of intra-molecular carboxylic anhydrides, peak at 171.9 ppm. The ester and acid carbonyls shift to 176.6 and 180.0 ppm respectively. Two methoxy groups are now observed at 72.3 and 74.6 ppm, which suggest that two different environments are present in the solid.

We also observed that after 15 days in water, in an ultrasonic bath, the insoluble fractions did not redissolve, indicating the formation of intermolecular crosslinks. Gelation can also occur during the shelf life of the polyelectrolytes solutions, in particular at concentrations above 50%. However, this gelation process is attributed to hydrogen bonding mechanisms without water loss. Solutions of (acryilic acid/methyl acrylate) copolymers are more stable than poly(acrylic acid) solutions at the same concentration but more viscous. The higher viscosity arises from the greater stiffness imposed to the poly-acid chains by the pendant methyl groups. This chain stiffness tends to prevent hydrogen bonding and gelation.[14]

Lyophilization of P-4 rendered 19% degree of crosslinking. Studies on the reactions occurring during lyophilization of 2-hydroxyethyl methacrylate , including the crosslinking, by NMR and FTIR are in progress. A preliminary result is shown in Figure 6.

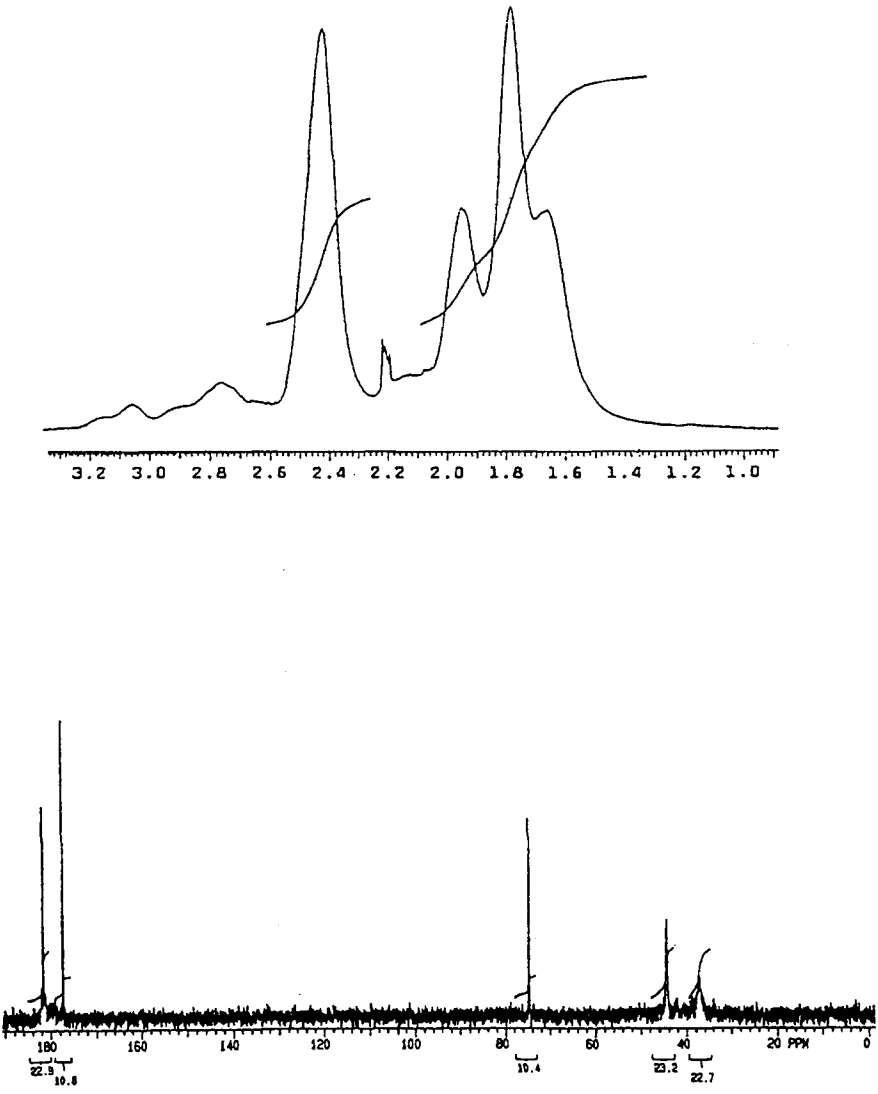

Figure 3. Spectra of P-3 sample in D_2O. a) 300 MHz ^1H NMR and b) 75 MHz decoupled ^{13}C with NOE suppressed.

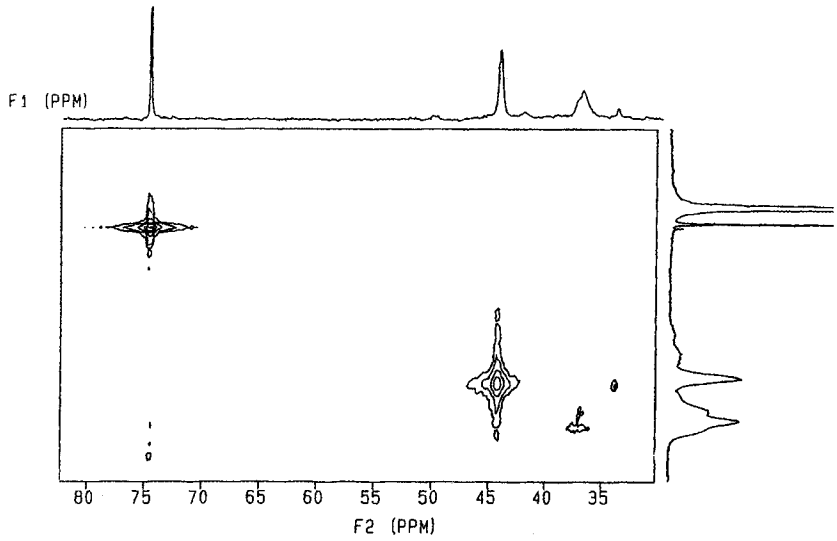

Figure 4. 200 MHz HETCOR spectrum of sample P-3 in D_2O.

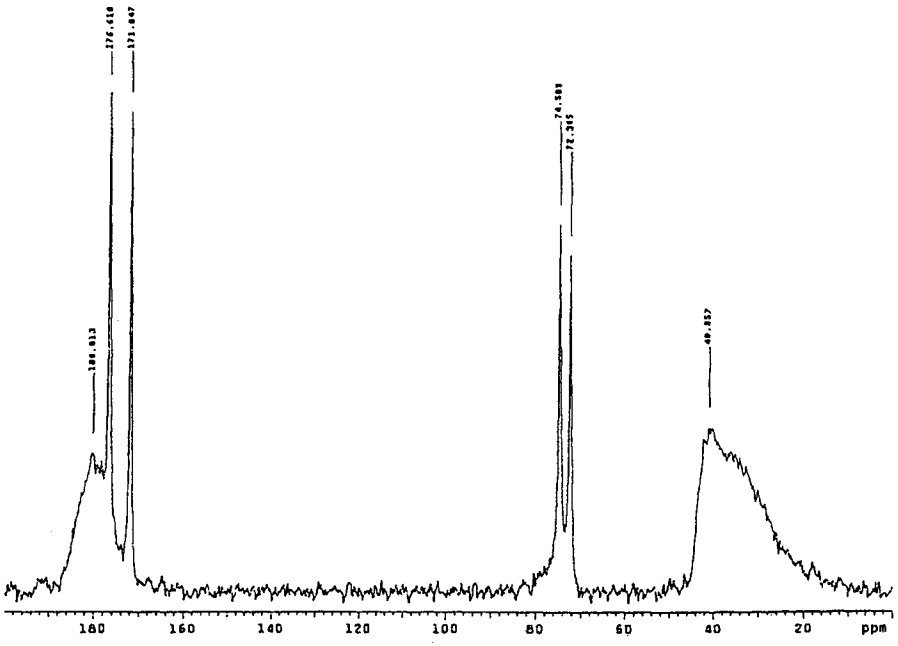

Figure 5. 75 Mhz ^{13}C CP-MAS spectrum of soluble fraction of lyopilized P-3 sample.

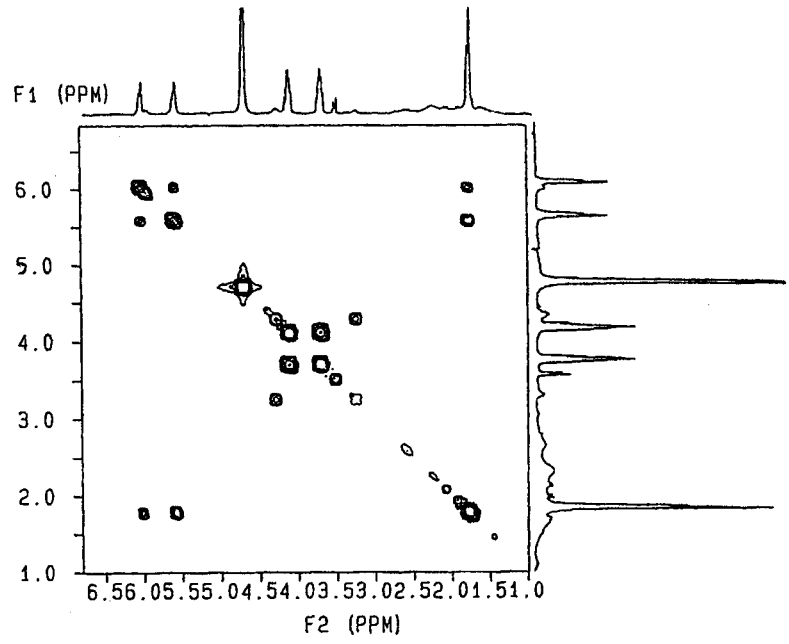

Figure 6. 200 MHz COSY spectrum of P-4 in D_2O

Molecular Parameters

The molecular parameters of each polymer were calculated as follows from the molecular weights (Table 1) and intrinsic viscosities. The values of **K** and *a* used in the Mark-Houwink equation are shown in Table 2 with the parameters *b*, σ, and *A*. From the obtained values of $[\eta]_\theta$ in both 1,4-dioxane at 30 °C and NaBr 1.5M at 15 °C, and $[\eta]$ in NaBr 0.1M at 25 °C, the linear expansion coefficient, α_η, was calculated (Table 3). By plotting the intrinsic viscosity vs. the molecular weight, the parameters K and B were obtained for each model (FFS, SF, IP, Be, and Kr) by using equations (12) to (17). From these, the other parameters, *A*, b, R_o, σ, and A_2 were calculated in theta and perturbed conditions.

The experimental intrinsic viscosities were compared with the calculated values. Maximum dispersions vary around 10%. The intrinsic viscosity of the polymers in 1,4-dioxane was also calculated from the $(M_v)_{GPC}$ elution fractions. A reasonable correspondence, 90% confidence,

was obtained with respect to the measured intrinsic viscosity in the same solvent. Correction factors for polydispersity were also used: In θ-conditions, 0.89 for (Mw/Mn) equal to 10, and 0.93 for (Mw/Mn) equal to 5. In perturbed conditions, 0.91 for (Mw/Mn) equal to 10, and 0.96 for (Mw/Mn) equal to 5. [18] By using these factors the difference between calculated and experimental data is less than 4%,

Table 2. Mark-Houwink constants **K** and *a*, and parameters b, σ and *A* for poly(acrylic acid).

SOLVENT	K x 10^4 dL/g	*a*	TEMP. °C	b, Å	σ	*A* X 10^{-4}, cm. ***
Anhydrous 1,4-dioxane *	8.50	0.500	30	5.65	1.83	730
NaBr 1.5M water solution**	12.40	0.500	15	7.40	2.38	825
HPLC grade1,4-dioxane *	6.60	0.600	30			(670)
NaBr 0.1M water solution**	3.12	0.755	25			(520)
NaBr 1.5M water solution ☆	11.70	0.500	15	7.60	2.04	809
HPLC grade1,4-dioxane ☆	6.46	0.600	30			(665)
NaBr 0.1M water solution ☆	5.24	0.755	25			(567)

* Ref. 8, ** Ref. 18, *** Equation (7), ☆ This work.

As expected, in theta-conditions the FFS, SF, and Be models yield about the same values for $\mathbf{K}_\theta$ and *A* as well as for *b* and σ for the PAA polymers, as shown in Table 2. In spite of the broad polydispersity shown by these polymers, the obtained values of $\mathbf{K}_\theta$ and *A*, are at most 7% below the reported values. Although equation (7) holds only for theta-conditions, the values of *A*, in perturbed conditions (shown in parenthesis in Table 2) were calculated from this equation for comparison. The IP model yields values well above those obtained from the others. This is expected because the IP model holds for high molecular weight polymers, which is not the case in this study, so it was excluded.

The expansion coefficients were calculated by using equation (9), taking for $[\eta]_\theta$ the values obtained in anhydrous 1,4-dioxane at 30 °C and for $[\eta]$ those obtained in NaBr 0.1M solution at 25 °C, the data are shown in Table 3. It can be observed that α increases with MW, from about 1.6 for low MW to 2.1 for high M.W. This behavior is predicted by theory.

The obtained values were compared with those obtained by taking the values of $[\eta]$ in non anhydrous 1,4-dioxane at 30 °C. The obtained values of α for polyacrylic acid were independent of molecular weight, and the mean value was about 1.13, indicating that they

should not be used to calculate α. Table 3 includes results obtained for other PAA samples of different molecular weights (PS series) prepared in the laboratory, for comparison.

Table 3. Intrinsic viscosities and expansion coefficients of acrylic polymers.

POLYMER	$(Mv)_{GPC}$	$[\eta]_\theta$, dL/g Anh dioxane 30 °C	[η],dL/g NaBr 0.1M 25 °C	[η],dL/g 1,4-dioxane 30 °C	$[\eta]_0$,dL/g NaBr 1.5M 25 °C	α
PS-8	369,000	0.516	4.980			2.12
PS-11	40,000	0.178	0.930	0.249	0.248	1.73
PS-12	23,300	0.129	0.619	0.184	0.189	1.68
PS-17	13,400	0.098	0.407	0.135	0.143	1.60
Paa-1	56,790	0.203	1.212	0.303	0.295	1.81
Paa-2	44,300	0.179	1.005	0.264	0.261	1.77
P-1	26,550	0.153	0.682	0.190	0.202	1.64
P-2	19,800	0.120	0.547	0.168	0.174	1.65
P-3	12,400		0.586	0.231		
P-4	4,650	0.151	0.455	0.188		

In perturbed conditions all models give different values for K. The FFS provides the closest approach with respect to reported values.[8,18] The calculated values of $\langle R_o^2 \rangle$ and $\langle R^2 \rangle$ both increase with molecular weight, and $\langle R^2 \rangle$ is greater than $\langle R_o^2 \rangle$ as expected. These values depend on those of A and α, so the FFS, SF, and Be models hold.

The weight-average MW of the PAA polymers in HPLC grade 1,4-dioxane, obtained by light scattering at about 27 °C differ from those obtained by GPC in 12% maximum. The value of A_2 is low (6.8×10^{-3} mol dL/g^2) while that obtained from equation (17) is of the same order of magnitude (4.7×10^{-3} mol dL/g^2).

The Mark Houwink parameters for the (acrylic acid/methyl acrylate) copolymer, sample P-3, were estimated by considering that the copolymer is a PAA with 66% of acrylic acid units (value obtained by NMR). Under this assumption, K equals to 6.15×10^{-4} dL/g and a to 0.062 at 30 °C in HPLC grade 1,4-dioxane. The intrinsic viscosities calculated from this parameters and the obtained from experimental measurements differ in about 9%. The estimated (A) is in range (654×10^{-11} cm).

The Mw of P-3 and P-4 are 12,400 and 4,500 respectively. These values represent an average of 100 repeating units of the copolymer and 45 of HEMA. Taking into account the lower limit recommended for MW determinations by intrinsic viscosity and for light scattering, the GPC technique is considered most useful for the MW determinations of these two polymers.

Conclusions

The dental materials P-1 to P-4 are low molecular weight polymers with broad polydispersity, as obtained by GPC. Bimodal distribution was observed for P-3 and P-4. One peak corresponds to the polymer and the other to a lower molecular weight compound.

Solution and solid state ^{1}H and ^{13}C-NMR, and FTIR confirmed the structure of poly(acrylic acid) in the model compounds and in P-2. The P-1 is mainly poly(acrylic acid) with an acrylic monomer in low proportion. The P-3 is a copolymer of (acrylic acid/methyl acrylate) with 2:1 composition as calculated from the NMR spectra. The P-4 is an oligomer derived from 2-hydroxyethyl methacrylate.

Initially, all samples were 100% water soluble. After lyophilization at -50 °C they showed different degree of solubility in water and in 1,4-dioxane because of cyclic anhydride formation and crosslinking.

The Flory-Fox-Shafgagen and the Stockmayer-Fixman models fits better the experimental data and can be used to describe the molecular parameters of the acrylic polymers in both theta and perturbed conditions.

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