# SYNTHESIS AND CHARACTERIZATION OF POLY (METHYL METHACRYLATE-STYRENE) COPOLYMERIC BEADS FOR BONE CEMENTS

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*Abstract*— **Acrylic bone cements have been used for about 40 years to fix artificial prosthesis to bone structure. The properties of the acrylic bone cement mostly depend on the characteristics of the beads, which are the main component of the solid part of the cement. In this work beads of poly(methyl methacrylate-co-styrene) were synthesized by suspension polymerization. The objective of this study was to obtain polymeric beads with particle size distributions and molecular weights that will permit the formulation of bone cements according to the international standards. Polyvinylpyrrolidone and polyvinylpyrrolidone-hydroxyapatite mixtures were studied as stabilizers of the system. Benzoyl peroxide (0.1, 1.0, 1.5% wt. in reference to the monomer) was the initiator of the reaction. The copolymeric beads were characterized by different analytical techniques. Polyvinylpyrrolidone alone was the best stabilizer and the bone cements prepared with polymer having low (247,000 g/mol) and high (800,000 g/mol) weight average molecular weights had static mechanical properties according to the requirements of commercial materials.**

*Keywords*— **bone cements, poly(methyl metha-crylate), suspension polymerization, mechanical properties.**

## I. INTRODUCTION

Acrylic bone cements are frequently used to fix the artificial prosthesis to the skeletal human system. The main application of bone cements is in the Total Hip Replacement. They have been used with this purpose for about 40 years (Charnley, 1964a, b). These materials main function are to secure of immediate anchorage of the implant and to permit a better distribution of body loads between the prostheses and the bone (Charnley, 1970; Planell *et al.*, 1995).

Acrylic bone cements are composed of two parts, a liquid part: methyl methacrylate (MMA), N,N-dimethyl-p-toluidine (DMT) and hydroquinone (Hq) and a solid part composed by: acrylic beads, usually poly(methyl methacrylate) (PMMA) beads or their copolymers, benzoyl peroxide (BPO) to initiate the polymerization reaction and frequently they also include a radiopaque agent such as barium sulfate, or zirconium oxide.

The setting and mechanical properties of the acrylic bone cement depend on the characteristics of the beads, which are the main component of the solid part of the cement (Lee *et al.*, 1973; Pascual *et al.*, 1996). The polymeric beads constitute about 70% by weight of the polymerized cement. The diameter of most of the acrylic particles used for bone cement ranges between 30 and 150μm (Planell *et al.*, 1995), however, there are reports where the average diameter varies between 10-30μm (Pascual *et al.*, 1996). The shape of the particles is related to the manufacture process used (Planell *et al.*, 1995). The molecular weight of the polymeric beads differs and depends on the cement commercial brand. The weight average molecular weight ($\overline{Mw}$) has values between $0.8 \times 10^5$ and $7 \times 10^5$ (Vila, 1992). It has been reported that some mechanical properties of the PMMA are independent of the molecular weight, for example abrasion and wear. Other properties such as tensile strength increases with the molecular weight up to $1.5 \times 10^5$ g/mol, above this molecular weight there is no change (Lautenschlager *et al.*, 1987)

Although there are some reports about the influence of the chemical composition, morphology, particle size distribution and molecular weight distribution in the final properties of the bone cement (Brauer, 1986, Zaldívar *et al.*, 1991; Morejón, 1992, Pascual *et al.*, 1996), the study of new stabilizers to obtain polymeric beads with optimal properties (morphology, particle size and distribution and polymer molecular weight and its distribution) is interesting because of its scientific and practical interest. In this work we analyzed the influence of the method to obtain the polymeric beads, on final properties of the bone cement. Copolymeric beads of poly(methyl methacrylate-co-styrene) P(MMA-ST) for bone cements were synthesized by suspension polymerization. In order to obtain adequate particle size distribution, two stabilizers of the suspension system were studied. We studied polyvinylpyrrolidone (PVP) as stabilizer of the suspension copolymerization of MMA and ST because by modifying its concentration

and molecular weight it is possible to obtain beads with different particle size distribution (Morejón, 1992). On the other hand this stabilizer is easy to remove from the beads surface, which is very important for the medical applications of the product. The other stabilizer system analyzed was a polyvinylpyrrolidone-calcium phosphate mixture. The aim of studying this stabilizer was to introduce calcium phosphate particles in a homogeneous way in the conventional formulation of bone cements. It responds to the interest to obtain a final product with bioactivity, capable of stimulate bone reorganization in the surrounding of the implant and which will allow to obtain a secure and more durable anchorage of the prosthesis. On the other hand, there are reports that mention that inorganic salts, for example, calcium phosphate powders, can provide an appropriate and clean stabilization of the monomer drops in the suspension polymerization for medical and industrial applications (Bishop, 1971). In this work the experiments were carried out with polyvinylpyrrolidone-hydroxyapatite (PVP-HA) suspensions. The HA was synthesized *in situ* previous to the polymerization by the reaction between $Ca(OH)_2$ and $H_3PO_4$.

Surgery materials should be sterilized and the sterilization process might change the molecular weight of the polymer and therefore its properties. For example, the Ethylene Oxide sterilization process does not affect the molecular weight of the polymeric beads but leaves residuals; on the other hand, Gamma Irradiation affects the molecular weight of the beads, but it is a clean technique. Then, it is very necessary to be able to obtain polymer beads with a wide spectrum of molecular weights in order to select the optimal composition depending on the sterilization method. For this reason another aim of this work was to obtain bone cements containing polymer with different molecular weight distributions and for this reason the influence of the initiator concentration on molecular weights was examined. The possibility for obtaining polymer with different molecular weight distributions will increases the spectrum of applications of these materials for different clinical cases

The P(MMA-ST) copolymeric beads synthesized were characterized by Optical Microscopy (OM), Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and Nuclear Magnetic Resonance (NMR-^{1}H, NMR-^{13}C). Bone cements were prepared using a conventional composition and employing a 2/1 solid/liquid volume ratio. Setting times and static mechanical properties (compression strength, tensile strength and fracture toughness) of the bone cement formulations were determined.

## II. MATERIALS AND METHODS

suspension polymerization was used to synthesize the acrylic beads. This technique consists on dispersing a monomer as droplets in a continuous phase and polymerizing in that way (Fig. 1). Usually an aqueous continuous phase is used and the monomer (s) is water insoluble. In our case the monomers are methyl methacrylate and styrene. We also used a suspension stabilizer and a vigorous stirring to maintain the stability of the system, that means avoid coalescence and agglomeration of the beads during the polymerization reaction. The ratio of methyl methacrylate/styrene monomers was 80ml/20ml. Stirring speed was 700 r.p.m. and reaction time was 24 h. The ratio of organic/aqueous phase was 1/3. Depending on the benzoyl peroxide concentration used (0.1, 1.0, 1.5 % of BPO) different temperature-time steps were used (Table 1). These temperature increment steps were used to prevent bead agglomeration and to obtain a high degree of conversion in order to minimize residuals of monomer and BPO. Table 2, shows the polyvinylpyrrolidone (PVP-K-90) and PVP-HA mixtures used as stabilizers.
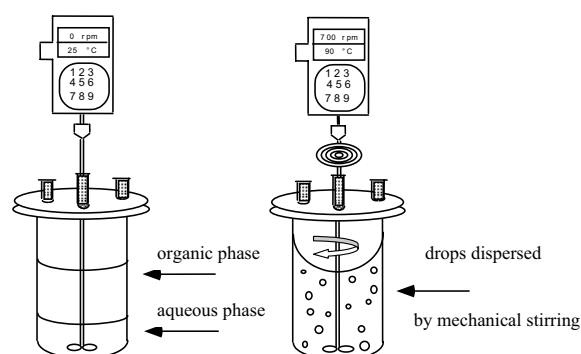


Figure 1. Schematic representation of suspension polymerization

Table 1. Temperature-time steps depending on the BPO concentration used

| | 0.1% BPO | 1.0% BPO | 1.5% BPO |
|---|---|---|---|
| | Temperature-Time | | |
| 24 h of reaction | 60 °C for 2 h | 60 °C for 2 h | 80 °C for 2 h |
| | 80 °C for 15 h | 80 °C for 15 h | 90 °C for 15 h |
| | 90 °C for 2 h | 90 °C for 2 h | 100 °C for 2 h |
| | 100 °C for 2:30 h | 100 °C for 2:30 h | 110 °C for 2:30 h |
| | 110 °C for 2:30 h | 110 °C for 2:30 h | 120 °C for 2:30 h |

Table 2. Polyvinylpirrolidone-hydroxyapatite mixtures

| PVP(%)* | HA (g) |
|---|---|
| 1.0 | 0 |
| 0.5 | 5 |
| 0.1 | 10 |
| 0.02 | 15 |

*Weight percent in reference to the aqueous phase

Optical Microscopy and Light Scattering were used to analyze the particle size distribution of beads. The molecular weight distribution was determined by Gel Permeation Chromatography (Perkin Elmer Chromatographer). The beads were examined by Differential Scanning Calorimetry (DSC) in order to determine the Tg values. The heating speed was 20 °C/min. The composition of the copolymer obtained

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was determined using NMR-$^1$H and NMR-$^{13}$C with a Varian Equipment Geminis 2000 at 200MHz in deuterated chloroform (5 %w/v) as solvent and tetramethylsilane (TMS) as internal standard.

## Bone cements formulations

The bone cement solid part was prepared with 88.0% (weight percent) of copolymeric P(MMA-ST) beads, 2.0% of benzoyl peroxide and 10.0% of barium sulfate. The liquid part had 99.0% (weight percent) of methyl methacrylate, 1.0% of N,N dimethyl-p-toluidine and 80 ppm of hydroquinone. In all cases an 2/1 solid/liquid ratio was used.

## Setting properties and Mechanical Assays

To determine setting time (St) and the temperature peak (maximum polymerization temperature, Tmax) the materials were mixed and put into an ultra high molecular weight polyethylene cylindrical mould, which was designed to obtain reproducible data using a minimum amount of cement mixture. The temperature was measured every 10 seconds with an $\Omega$ Omega$^®$ DP465 Silver Plated thermocouple inserted in the center of the mass volume. The setting time was calculated as the time when the temperature reaches the value:

$$T = \frac{T_{max} + T_{env}}{2}, \quad \text{being} \quad T_{env} \quad \text{the enviromental}$$

temperature.

The compression strength of the cement was determined according to the specifications of ISO-5833 standard (ISO 5833, 2002). The specimens dimensions were 12 mm and 6 mm in height and diameter and the tests were carried out at a constant cross-head speed of 20mm/min. The tensile strength experiments were carried out using halterium plane probes elaborated according to the ASTM-638 standard (ASTM D 638, 1991). The dimensions of the test specimens are shown in Fig. 2. The cross-head speed employed was 1 mm/min. Compression and tensile testing were carried out in a United 5802 Universal Testing Machine. Each sample was measured and stored for 24 ± 2 h in dry conditions at 23 ± 2 °C prior testing. At least five specimens were tested, and the mean and standard deviation is reported for each sample.

Fracture toughness was measured using compact tension (CT) test specimens prepared following ASTM 5045 standard (ASTM D5045, 1999). The cement formulations were prepared at room temperature and were manually inserted into a teflon mould at approximately dough time. The mould was closed and the mixture was kept there for one hour at 37 ± 0.1 °C. The blocks obtained were subsequently machined to the specified dimensions (Fig. 2). The notch tip was sharpened with a razor blade. The tests were performed after a month of sample preparation using a Universal Testing Machine BIONIX 858 Test System MTS with an elongation speed of 1 mm/min. The fracture toughness, $K_{1c}$, corresponding to elastic-plastic fracture mechanics conditions is given by:

$$K_{1c} = \frac{f(a/W) * P_{max}}{B * W^{1/2}}, \tag{1}$$

where $P_{max}$ is the peak load during the test, B is the thickness of the specimen and $f$(a/w) is a geometrical factor. In all cases it was verified the fulfillment of conditions of plane deformation in the crack tip (Hertzberg,1996):

$$B, a, (W - a) > 2.5 \left[ \frac{P_Q}{\sigma\sigma_{ys}} \right]^2, \tag{2}$$

where $\sigma_{ys}$ is the elastic limit stress and $P_Q$ is found by the intersection of the stress-strain curve with a secant line having a slope 5% lower than that of the linear region. $f$(a/w) was calculated by:

$$f(X) = \frac{(2 + X)}{(1 - X)^{3/2}} \left[ 0.886 + 4.64(X) - 13.32(X)^2 + 14.72(X)^3 - 5.6(X)^4 \right],$$
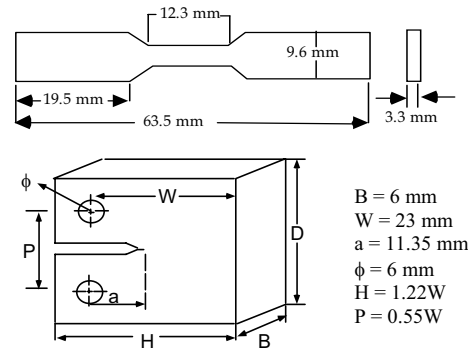
where $X = a/W$.



B = 6 mm
W = 23 mm
a = 11.35 mm
$\phi$ = 6 mm
H = 1.22W
P = 0.55W

Figure 2. Tensile and Fracture Toughness specimens dimensions.

## III. RESULTS AND DISCUSSION

### Particle Size Distribution

Morphologic analyses of the beads showed that the particles were spherical for both stabilizers. When using PVP as stabilizer, beads with clean surfaces, unimodal particle size distribution and average diameters between 24 and 34 μm (which are on the range of particle size of commercial materials) were obtained (Fig. 3a.)

When using PVP-HA as stabilizer particle size distribution was bimodal and the average size of the beads was higher than 100 μm fact that makes difficult the handle of the bone cements (Fig. 3b). Larger size was obtained because the amount of PVP was reduced and the HA was not as effective as the PVP as stabilizer. The surface of beads had inlays of HA. Optical Microscopy indicated that the higher concentration of HA as stabilizer, the higher amount of HA particles

adhered to the beads surfaces. This is shown in Fig. 4, where the beads were completely covered with HA in a 0.02% PVP-15g HA system as stabilizer. The fact that the polymeric particle size was excessively increased when using the PVP-HA stabilizer in all formulations, limits the use of calcium phosphate as a suspension stabilizer of the beads for bone cements. For this reason we only increased the concentration of HA in the PVP-HA mixtures as stabilizer until 15g (Table 2).
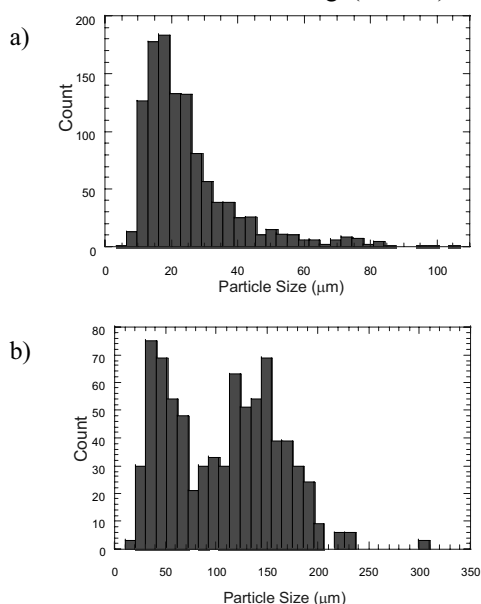
a)

b)

Figure 3. Particle size distribution of the copolymeric beads. a) 1.0% PVP (P3). b) 0.1%PVP-10gHA (P6).
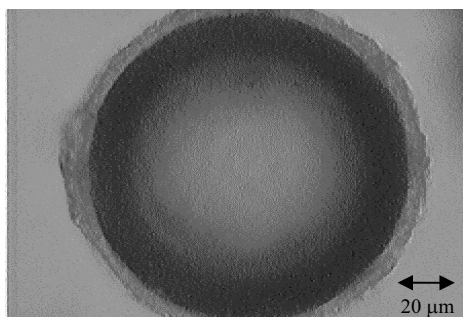

Figure 4. Optical Microscopy of a P(MMA-ST) bead obtained with 0.02% PVP-15g HA.

Table 3. Number average diameter and Size Range of the P(MMA-ST) beads obtained with different initiator concentration (BPO) and different stabilizer system.

| Stabilizer | Polymer | Average diameter (μm) | Range (μm) |
|---|---|---|---|
| 1.0% PVP | P1 (0.1%BPO) | 24.3 | 3-123 |
| | P2 (1.0%BPO) | 28.5 | 5-95 |
| | P3 (1.5%BPO) | 33.9 | 10-120 |
| 0.1%PVP-10.0g HA | P4 (0.1%BPO) | 101.8 | 6-280 |
| | P5 (1.0%BPO) | 108.5 | 6-350 |
| | P6 (1.5%BPO) | 120.6 | 10-430 |

Table 3 presents the number average diameter of beads obtained with 1.0% PVP and 0.1% PVP-10.0g

HA mixtures at different concentration of initiator (BPO). It is observed a slight increment in the average diameter with the increment of initiator concentration but there were no statistical differences. The beads obtained when using HA as stabilizer were too big for to be used as part of the formulation of bone cements.

**Molecular Weight Distribution**
As expected, the molecular weight of the polymer decreases with the increase of initiator concentration due to the higher concentration of free radicals in the system. Under the studied conditions, average weight molecular weights ($\overline{Mw}$) between 232 000 and 850 000 g/mol (Table 4) were obtained. In all cases molecular weight distributions were unimodal and polydispersity values between 1.6-3.4 were obtained.

Table 4. Average Molecular Weight (g/mol) of P(MMA-ST) beads according to initiator concentration and stabilizer type for two batch of each system

| Stabilizer | Sample | $\overline{Mn}$ | $\overline{Mw}$ | $\overline{Mz}$ | $\overline{Mw}/\overline{Mn}$ |
|---|---|---|---|---|---|
| 1.0% PVP | P1 (0.1%BPO) | 215 000 | 850 000 | 1 530 000 | 3.38 |
| | | 270 000 | 700 000 | 1 580 000 | 2.59 |
| | P2 (1.0%BPO) | 174 000 | 369 000 | 878 000 | 2.12 |
| | | 160 000 | 350 000 | 825 000 | 2.18 |
| | P3 (1.5%BPO) | 109 000 | 232 000 | 510 000 | 2.12 |
| | | 150 000 | 247 000 | 473 000 | 1.64 |
| 0.1% PVP-10.0g HA | P4 (0.1%BPO) | 232 000 | 512 000 | 930 000 | 2.20 |
| | | 220 000 | 625 000 | 850 000 | 2.84 |
| | P5 (1.0%BPO) | 186 000 | 343 000 | 615 000 | 1.84 |
| | | 131 000 | 355 000 | 683 000 | 2.70 |
| | P6 (1.5%BPO) | 108 000 | 263 000 | 478 000 | 2.43 |
| | | 97 000 | 242 000 | 425 000 | 2.49 |

Figure 5 shows the differential molecular weight distributions as a function of the initiator concentration when using 0.1%PVP-10.0gHA experiments. It can be seen that the distributions are unimodal and that molecular weight increases with the decrease of the initiator concentration. By comparison the average molecular weight for the solid part of the commercial bone cement Surgical Simplex P was determined: $\overline{Mn}$ = 9.98 *10^4 g/mol, $\overline{Mw}$ = 2.32 *10^5 g/mol, $\overline{Mz}$ = 3.63 *10^5 g/mol.

Taking into account the obtained results, the subsequent studies (characterization studies, preparation of bone cement formulations, and mechanical assays) were carried out with P1 and P3 samples which were samples with adequate size particle distributions and extreme (the highest and the lowest) values of average molecular weight. It was verified that the cement formulations produced homogeneous dough and were easily handled. The manipulability characteristics of each cement composition have a special importance, because they are a qualitative parameter that allows identifying whether those compositions can be used for practical formulations.
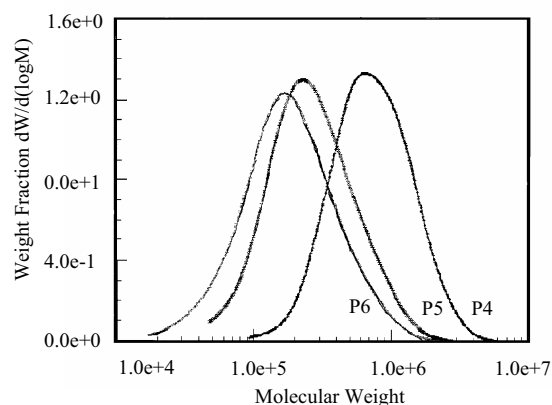
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Figure 5. Differential molecular weight distribution as a function of initiator concentration when using 0.1%PVP-10.0g HA stabilizer

**Spectroscopic Characterization of the P(MMA-ST) beads.**

The synthesized P(MMA-ST) beads were characterized by NMR-$^1$H, and NMR-$^{13}$C. Figure 6 shows a typical NMR-$^1$H spectrum of the copolymeric beads which corresponds to the statistical distribution of the monomeric units along the copolymer chains (Aerdts *et al.*, 1993). The copolymer composition was determined by comparing integrated intensities of resonance signals and chemical shifts, Table 5.
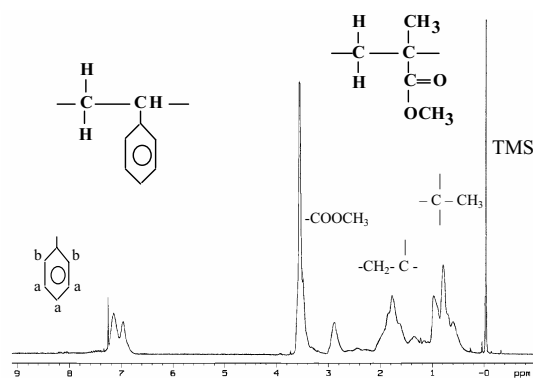


Figure 6. NMR-$^1$H spectrum of P3 beads

The monomeric distribution in the polymeric chain depends on the reactivity ratios $r_1 = k_{11}/k_{12}$ y $r_2 = k_{22}/k_{21}$, where $k_{11}$ and $k_{12}$ are the specific rate constants of homopolymerization and $k_{12}$ and $k_{21}$ are the specific rate constants of copolymerization. In the radicalic copolymerization of MMA and ST the reactivity ratios are very similar: 0.46 and 0.52 at 60°C, and 0.59 and 0.54 at 131°C respectively (Odian, 1991). The reactivity ratios are inferior to the unit, which indicates that each monomer has a natural tendency to react with the other monomer. However, for the reaction studied there is a larger amount of methyl methacrylate monomer in the feed mixture (80MMA/20ST) and the reaction is not carried out in conditions that allow a strict alternation of

the monomers. For this reason the polymer obtained was statistical.

Table 5. NMR-$^1$H chemicals shifts and signal assignations of P3 beads.

| Chemical Shifts ($\delta$) | Assignation |
|---|---|
| 7.15 | Aromatic Protons |
| 6.97 | a 3 (metha and para) protons |
| | b 2 protons (orto) |
| 3.56 | -COOCH$_3$ Protons |
| 2.88 | -COOCH$_3$ Protons |
| 1.77 | -CH$_2$ methylene protons |
| 1.0-0.5 | -CH$_3$ Methylic Protons |

The fact that the polymers have a statistical distribution of the monomers along the chain means that an important spatial regularity is not probable. If a polymer is perfectly alternated MMA-ST, it can be stated that they have three types of space isomerism for each triad: MMA-ST-MMA, or, ST-MMA-ST (Fig. 7).
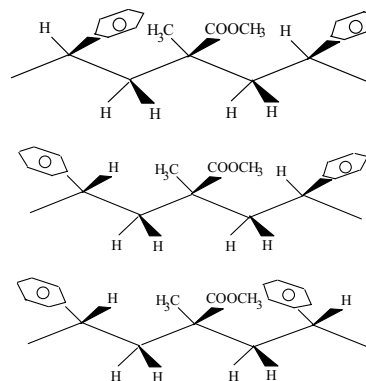


Figure 7. Space isomerism of ST-MMA-ST triad.

However, for a statistical polymer 20 space configurations existed, 10 for the triads centered in styrene and 10 for the triads centered in methacrylate with different configurational sequences, for example: centered triads in MMA:

MMA-MMA-MMA: $\sigma_{mm}^2 F_{MMM}$,
$2\sigma_{mm}(1-\sigma_{mm})F_{MMM}$,
$(1-\sigma_{mm})^2 F_{MMM}$)

MMA-MMA-ST
ST-MMA-MMA
$\sigma_{mm}\sigma_{ms} F_{MMS}$,
$(1-\sigma_{mm})\sigma_{sm}F_{MMS}$,
$\sigma_{mm}(1-\sigma_{sm}) F_{MMS}$,
$(1-\sigma_{mm})(1-\sigma_{sm})F_{MMS}$

ST-MMA-ST
$\sigma_{sm}^2 F_{SMS}$,
$2\sigma_{sm}(1-\sigma_{sm})F_{SMS}$
$(1-\sigma_{sm})^2 F_{SMS}$,

where: F is the molar fraction for each type of triad and $\sigma$ is named coisotacticity parameter and it is the probability that two monomeric units have isotactic

configuration. It is reported (Aerdts *et al.*, 1993) that σ has the following values: $\sigma_{mm}=0.23$, $\sigma_{ss}=0.29$, $\sigma_{sm}=0.44$.
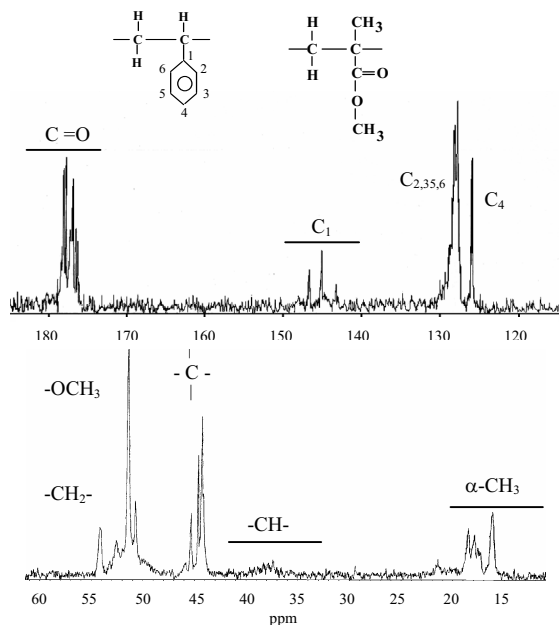


Figure 8. NMR-^{13}C spectrum of P3 beads.

The NMR-^{13}C spectra showed tree types of stereoisomers (Fig.8). The $\alpha$-CH$_3$ and C$_1$ groups indicated the presence of these three different relative positions in the space of the groups. In the case of $\alpha$-CH$_3$ groups four picks denominated A,B,C,D: A, 23.0-21.2 ppm; B, 21.2-19.8 ppm; C, 19.8-17.8 ppm; D, 17.8-16.5 ppm can be seen. In this case, the assignation of the signal is not clear. However, the C$_1$ signal is divided in three picks, the assignation in this case is already reported (Maxwell *et al.*, 1993): X, 147.5-146.8ppm Sindyotactic; Y, 146.8-145.15ppm Atactic and Z 145.15-143.5ppm Isotactic (Fig. 9). In this way it can be concluded that in the synthesized polymer there are three space configurations: Syndiotactic, Atactic and Isotactic. Table 6 summarizes the NMR-^{13}C chemicals shifts and signal assignations.

The glass transition temperature (Tg) determined for the P1 and P3 polymer samples were $112.5\pm 1.2°C$ and $112.9\pm0.8°C$ respectively, which confirms that the spatial structure is due to a space isomers mixture. Other authors reported (Encyclopedia of Polymer Science and Engineering, 1985) that the Tg values were 105 °C for Atactic, 160 °C for Syndiotactic and 43 °C for Isotactic copolymers. For bone cement materials 52.6% of Syndiotactic, 37.42% of Atactic and 3.6% of Isotactic isomers have been described (Stupp and Yau, 1981).

Another conclusion that is derived from the Tg values is that there are not significant differences between the P1 and P3 structures although the average molecular weight $\overline{Mw}$ of P1 is three times higher than

the average molecular weight $\overline{Mw}$ of P3. Some reports indicate that certain polymeric properties become independent of the molecular weight starting from certain values (Lautenschlager *et al.*, 1987).
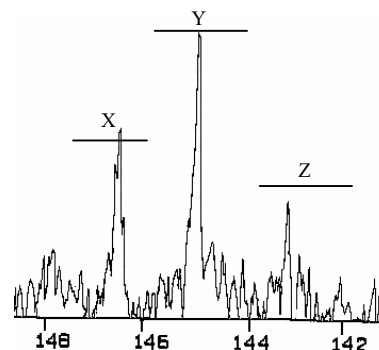


Figure 9. C$_1$ signal amplified zone of the NMR-^{13}C spectrum of P3 beads

Table 6. NMR-^{13}C chemicals shifts and signal assignations

| Structure | Chemical Shift (δ) | Signal | Chemical Shift (δ) | Signal |
|---|---|---|---|---|
| | 177 | C=O | 47-44 | -C- -CH- |
| | 147.5-146.8 | C$_1$ | 39-37 | -C- -CH- |
| | 146.8-145.15 | C$_1$ | 23.0-21.2 | $\alpha$-CH$_3$  A |
| | 145.15-143.5 | C$_1$ | 21.2-19.8 | $\alpha$-CH$_3$  B |
| | 130-121.7 | C$_{2,3,5,6}$ | 19.8-17.8 | $\alpha$-CH$_3$  C |
| | 126 | C$_4$ | 17.8-16.5 | $\alpha$-CH$_3$  D |
| | 55-47 | -OCH$_3$ + -CH$_2$- | | |

**Setting Time and Temperature Peak.**
Curing of the acrylic cement is a complex process because the contact between the liquid and the solid part marks the onset of several physical and chemical events that take place simultaneously. The solvation of the polymeric beads by the monomer, dissolution of the free radical initiator, diffusion from the liquid to the solid phase and monomer evaporation from the mixture are some of the physical events that occurs (Lautenschlager *et al.*, 1987). The most important chemical process is the free radical polymerization of the MMA. Furthermore, due to the presence of hydroquinone and oxygen (inhibitors), which capture the free radicals produced by the initiator, there is always present an induction time. After inhibitors are consumed, polymerization reaction starts, the monomer is rapidly consumed by the propagation rate and the viscosity increases, producing an increment in reaction rate and in temperature because of the so called "gel effect" (Odian, 1991). The viscosity of the curing mixture

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increases rapidly because of the dissolution of the beads of PMMA (the smaller the beads, the larger the ratio of surface area/volume, the faster their dissolution and the larger the molecular weight the larger the increase in viscosity) and by the conversion of the monomeric units into large polymeric chains. Therefore, the setting time of the curing of acrylic cements depends on diverse factors, among them: the initiator and inhibitors concentration of the formulation, the properties of the polymeric beads (particle size and molecular weight distribution) that determined the proportion of polymer dissolved in the monomer and of course the humidity and the environmental temperature. According to the ISO and ASTM international standards the setting time of the acrylic bone cement should be between 3-15 min and 5-15min respectively. The polymerization of acrylic bone cement is an exothermic reaction and the calculated heat of polymerization of MMA is 544J/g (Meyer *et al.*, 1973). The thermal effects of the polymerization are reflected in a significant temperature peak (ranging between 80°C and 124°C in the cement (Saha and Pal, 1984) and between 48°C and 105°C at the bone/cement interface (Brauer *et al.*, 1986). It has been reported that the polymerization temperature of acrylic bone cement can cause necrotic areas in the surrounding of the prosthesis (Meyer *et al.*, 1973). The thermal damage in the bone can affects the durability of the implant, because it induces bone reabsortion and produces aseptic loosening of the prosthesis. In order to minimize the thermal necrosis of the adjacent tissues and to promote a long-time good fixation the international standards established that temperature peak of bone cement curing should not overcome the 90ºC. The values of the setting time and the temperature peak obtained from the experiments are shown in Table 7. It can be seen that temperature peaks are low, which is important to prevent tissue damage. Similar setting times were obtained for both formulations. However, since that particle size is smaller (and molecular weight is larger) for P1 than for P2, then the medium viscosity will be higher. This results in a bigger "gel effect" and a higher temperature peak. Both samples fulfill the requirements of setting time and the temperature peaks of polymerization are low.

**Mechanical Testing**

Adequate mechanical properties of bone cements are essential to avoid the failure of the hip prosthesis during their use. There are numerous reports in the scientific literature about these properties. For the commercial cements they report the following values: Compression strength: 77 to 103 MPa (Freitag and Cannon, 1976; Hansen and Steen, 1992; Topoleski *et al.*, 1993; Kühn, 2000), Tensile strength: 24.5-64.9 MPa (Lee and Ling, 1975; Pilliar *et al.*,1976; Pourdeyhimi and Wagner, 1989) and Fracture Toughness: 0.87 to 1.59 MPa m$^{1/2}$ (Freitag and Cannon, 1976; Starck, 1979; Sih and Berman, 1980; Vila *et al.*, 1990). In Table 7 mechanical properties of the cements are presented. In all cases the cement samples overcome the minimum requirements of the standards and they are in agreement with the values reported for commercial materials. The results obtained here show that in the range of molecular weights studied 230 000-850 000 g/mol the mechanical properties are independent of molecular weight of the polymer in the beads

This work demonstrates that it is possible to obtain a wide range of molecular weights for the P(MMA-ST) beads that satisfy the required mechanical properties. This method is effective to prepare P(MMA-ST) beads for different medical applications. Also, this technique allows obtaining beads containing polymer with an appropriate molecular weight for a specific sterilization method.

Table 7. Properties of experimental bone cements

| Assay | P1 | P3 |
|---|---|---|
| Tmáx (°C) | 45.6 ± 5.9 | 38.0 ± 6.6 |
| Setting Time (min) | 7.9 ± 0.4 | 7.9 ± 0.7 |
| Compression Strength $\sigma_c$ (MPa) | 97.1 ± 0.6 | 97.8 ± 1.2 |
| Compression Elastic Modulus, $E_c$ (GPa) | 1.5 ± 0.2 | 1.66 ± 0.05 |
| Tensile Strength $\sigma_t$ (MPa) | 37.0 ± 3.1 | 34.0 ± 3.1 |
| Tensile Elastic Modulus, $E_t$ (GPa) | 2.1 ± 0.1 | 2.1 ± 0.4 |
| Fracture Deformation, $\varepsilon$ (%) | 2.3 ±0.1 | 1.9 ± 0.2 |
| Fracture Toughness, $K_{Ic}$ (MPa m$^{1/2}$) | 1.66 ± 0.04 | 1.65 ± 0.20 |

## IV. CONCLUSIONS

It was demonstrated that the two stabilizers studied (PVP and PVP-HA mixtures) are effective to avoid the coagulation during the suspension polymerization process to obtain P(MMA-ST) beads. However, though the morphological analysis revealed spherical particles when using both stabilizers, only PVP provides the beads with unimodal distribution in the range of sizes of commercial cements: 10-30 μm. In the case of the PVP-HA stabilizer the distribution obtained is bimodal and the average bead size is higher than 100 μm. This excessive bead size prevents the use of this stabilizer in the synthesis of beads for acrylic bone cements. With initiator concentrations between 0.1-1.5% and under the reaction conditions used, polymers with weight average molecular weights ($\overline{Mw}$) in a range between 230 000 and 850 000 g/mol were obtained, which is very useful for the preparation of cements for different medical applications. In all cases the molecular weight distributions were broad, symmetrical and unimodal. The polydispersity values were between 1.6 and 3.4. The experimental bone cements have setting and mechanical properties in agreement with the requirements of international standards.

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