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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Influence of Stirring Speed on the Suspension Copolymerization of Styrene with Methyl Methacrylate

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To cite this Article Cordoví, Carlos M. , De Lucas, Antonio , Rodríguez, Juan F. and Tejada, Juan(1997) 'Influence of Stirring Speed on the Suspension Copolymerization of Styrene with Methyl Methacrylate', *Journal of Macromolecular Science, Part A*, 34: 8, 1339 – 1351

To link to this Article: DOI: 10.1080/10601329708011048

URL: <http://dx.doi.org/10.1080/10601329708011048>

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INFLUENCE OF STIRRING SPEED ON THE SUSPENSION COPOLYMERIZATION OF STYRENE WITH METHYL METHACRYLATE

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ABSTRACT

The influence of stirring rate on the suspension copolymerization of methyl methacrylate-styrene system was studied. A significant growth of particle size during the copolymerization reaction takes place. It was found that the increase of stirring rate produces a reduction of particle size, being possible to relate the final average particle size to the stirring rate. The kinetic of copolymerization reaction corresponds to that of bulk free radical initiated polymerization and it is not affected by the stirring rate. Copolymerization composition and average molecular weight distribution are in reasonable agreement with the data reported in the literature for the same monomer systems in bulk polymerization. This copolymer

shows enhanced thermal stability compared to methyl methacrylate polymers.

INTRODUCTION

Presently, styrene-methylmethacrylate copolymers (SMA) are being used to make clear ABS-type polymers and others industrial applications [1]. The perspectives of using such polymers as new biomaterials for its use in human healthcare, open a new field of application of these polymeric materials. This biomaterial is basically constituted by a SMA copolymer powder and other pharmaceutical compounds.

In order to reach a product with the adequate clinical properties, SMA copolymer must be prepared by suspension polymerization, as a powder with a mean diameter of 50 μm . Therefore, the main problem is to achieve an adequate particle size distribution in the final product. The molecular weight distribution and the relation between the monomer units in the SMA copolymer are also critical factors for this new application.

Control of size and uniformity of polymer beads has become a major area of interest because products with a controlled and defined size meet the enhanced requirements of many applications [2]. Traditionally, the conventional method of preparation of polymer beads is suspension polymerization in a jacketed reactor with an anchor type agitator. Typically, bead sizes range from 5 μm to 5 mm [3]. In the suspension polymerization of styrene, Konno et al. [4] reported values of Sauter diameter ranging between 400 and 800 μm for different experimental conditions. Recently, Alvarez, et al. [5] have developed a mathematical model to describe the particle size distribution of a suspension polymerization of styrene. Nevertheless, in order to obtain a narrow size distribution, the working conditions have to be often fitted to each practical application and non-standard polymerization devices such as loop reactors, vibrating nozzles, rotating disks and similar equipment, have been developed [6,7].

In the simple case of a polymer that is miscible in all proportions with its monomers (as in our case), various viscosity states of the disperse phase are traversed during the course of polymerization. The initially nonviscous, liquid monomer mixture is transformed gradually into a increasingly viscous solution of polymer in monomer, and as a conversion proceeds the disperse phase acquires the characteristic of a solid polymer, this is known as the particle identity point [8,9].

During the initial and intermediate sticky stages, the energy introduced into the reactor per unit time is the main factor that will finally determine the particle size distribution. Other factors that exert an important influence on particle size and size distributions will be the shape and dimensions of the reactor and stirrer, the temperature, the intensity of stirring and the type and concentration of the stabilizer [10-14]. The present work deals with the suspension copolymerization of styrene with methyl methacrylate. The influence of stirring rate on the particle size distribution, molecular weight distribution, polymerization rate and polymer composition was investigated.

EXPERIMENTAL

Material

Styrene and methyl methacrylate (FLUKA, Reagent Grade) were freed from inhibitor by washing with sodium hydroxide solution (5% weight) followed by several washings with water. Polyvinylpyrrolidone (M.W: 360000, FLUKA) was used as dispersant in solution of 1% and 10% by weight to avoid drop coalescence in the taken samples. Benzoyl Peroxide (FLUKA, Reagent Grade) was used as initiator. Sodium hydroxide, methanol and calcium chloride (FLUKA, Reagent Grade) were used as additional reagents.

Polymerization Procedures

Suspension copolymerizations were carried out in a 2 l double jacketed glass reactor equipped with digital control of stirring rate and temperature. Small aliquots (5-8 g) of the suspension were periodically taken and poured in a 10% solution of polyvinylpyrrolidone to avoid coalescence of droplets before the identity point.

The experimental set up is shown schematically in Figure 1. A stirrer with four vertical blades was used. Dimension parameters of the equipment are also shown in Figure 1.

The following recipe for suspension copolymerization was used:

| Compound | % Weight |
|----------------------|----------|
| Styrene | 18.97 |
| Methyl Methacrylate | 4.55 |
| Water | 75.475 |
| Benzoyl Peroxide | 0.251 |
| Polyvinylpyrrolidone | 0.754 |

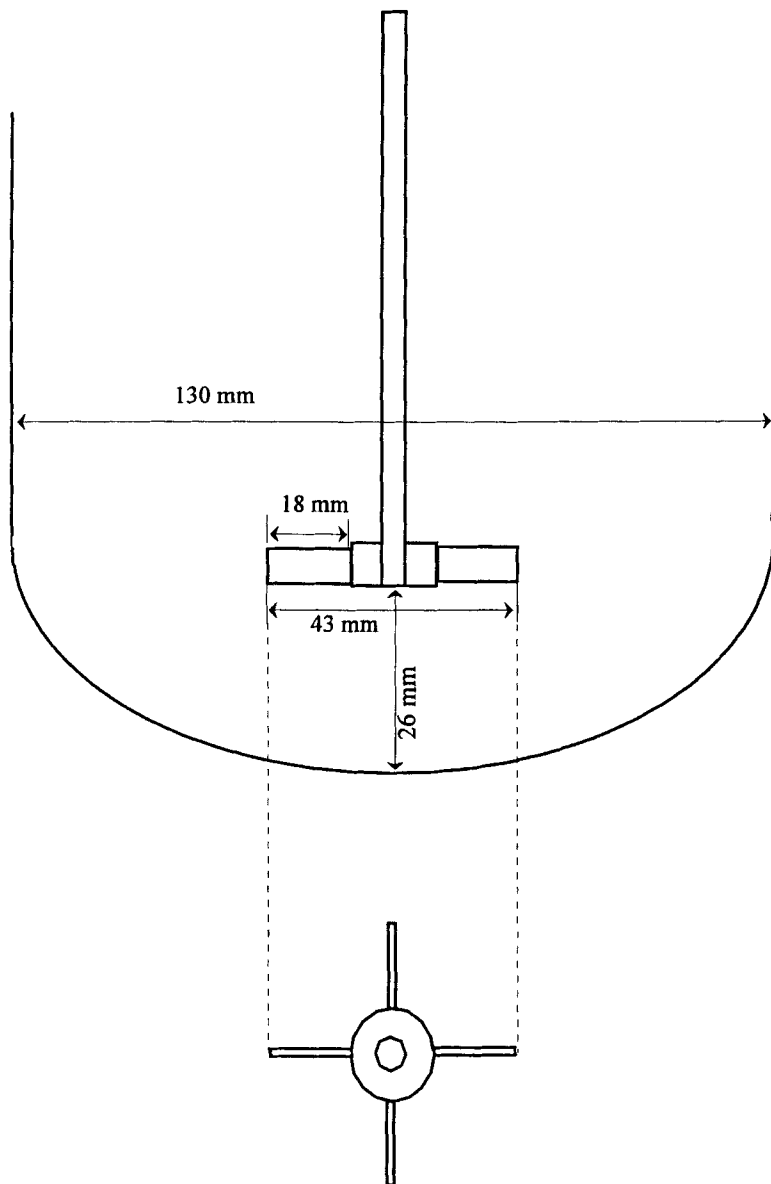


Figure 1. Temperature profiles during the suspension copolymerization process.

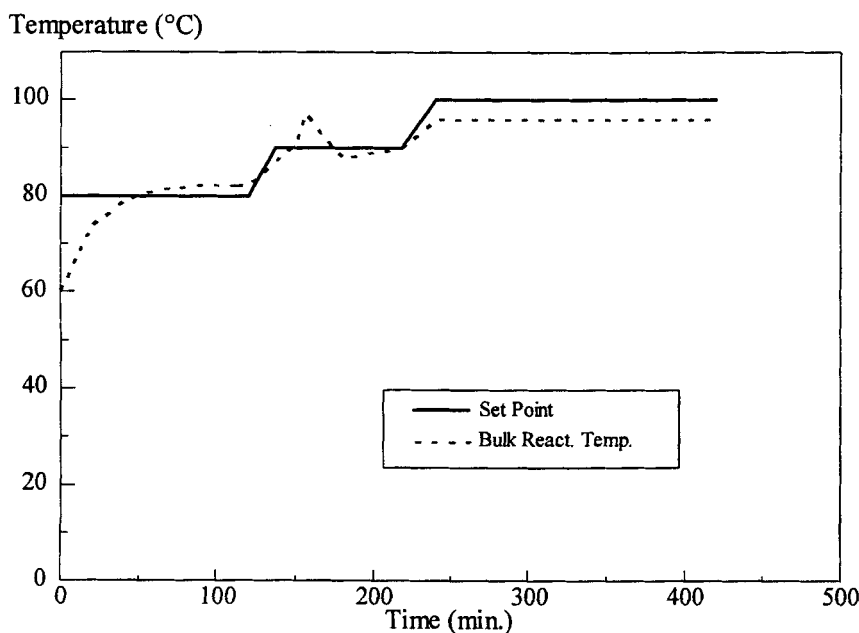


Figure 2. Detail of the experimental device with indication of equipment dimensions.

Temperature was not in a fixed value during the experiments. In a typical run, 895 g of the aforementioned reaction mixture was charged into the reactor and heated, while stirring, until reaching 60°C. This point was considered as zero time. Then, set point of the temperature controller was risen at 80°C for two hours. Later, temperature set point was maintained at 90°C for two hours and finally at 100°C for the last three hours. As an example, temperature profile inside the reactor is shown in Figure 2 for the run of 400 rpm.

The composition of the copolymer and the temperature profile were initially established in a prospective study dealing with the feasibility of using such S-MMA copolymers as bone binder. The biological compatibility of such materials was demonstrated [15]. While the temperature profile could be slightly modified in this experimental work, the composition of the biomaterial had to be maintained identical, in order to ensure its suitability.

Measurements

The change of particle size distribution during the copolymerization process was determined from several microphotographs of each stabilized sample. After

that, a statistical treatment of the experimental measurements was done using commercial and self developed programs (Statgraphics, Excel). Number average diameter, Sauter diameter and weight average diameter (only for the final samples) were calculated for each sample, using the following expressions:

The weight average diameter of final solid copolymer particles was also measured using a Sedigraph 5100 (Micromeritics) apparatus, corroborating the values obtained from microphotograph.

Number and weight average molecular weights (\overline{M}_n and \overline{M}_w , respectively) and polydispersity ($\overline{M}_w / \overline{M}_n$) of the copolymer were determined by gel-permeation chromatography (GPC) at 38°C. GPC measurement was carried out on a LC Waters mod. 150-GPCV at a flow rate of 1 ml/min using tetrahydrofuran as diluent. ^1H NMR spectra were recorded on a Varian Unity 300 operating at 299.89 MHz. Deuteroacetone and tetramethyl-silane were used as solvent and internal standard, respectively. Curves of thermal decomposition were obtained on a Perkin Elmer thermogravimetric analyzer mod. TGA 7.

RESULTS AND DISCUSSION

Figure 3 shows the evolution of number average diameter of droplets during the polymerization for different stirring rates ranging between 400 and 600 rpm. It can be seen that particle size increases as reaction progresses, until reaching a certain maximum value. This final value is attained at a certain time, the identity point, in our case between 150 and 180 minutes from the beginning of the experiment.

The increment of particle size during a suspension polymerization has been reported and explained by several authors [4,5,16,17]. There are basically two kinds of behaviors in suspension polymerization [1]:

A. System in which the final particle size is already established at very low conversion. Polymerizing droplets maintain their identity along the experiment, and subsequent reduction in a stirring speed has no influence on particle size.

B. Systems in which the particles reach the so-called identity point only at high conversion.

With these systems it is apparently necessary to take into account the time and conversion dependence of the parameters affecting the polymerization. In certain systems of this kind, the stirring time in which the unpolymersed emulsion reaches its final droplet diameter is higher than that employed by the polymerizing system to reach 50% conversion.

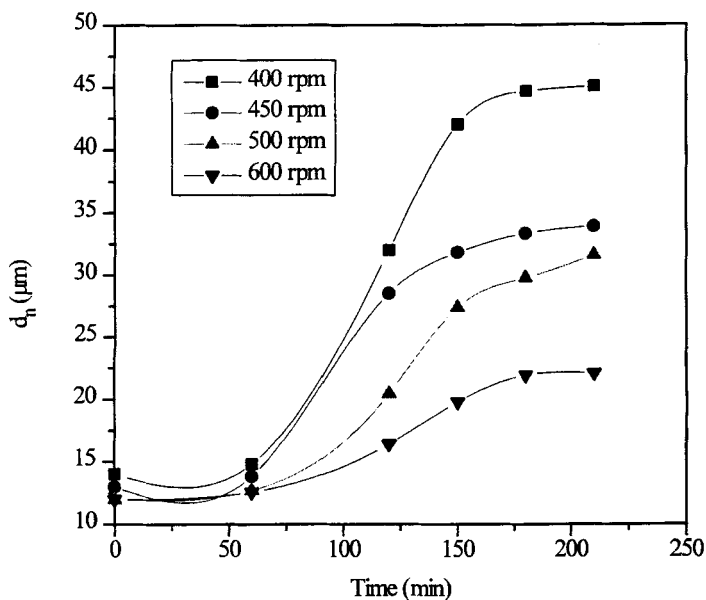


Figure 3. Suspension copolymerization of methyl methacrylate and styrene. Influence of stirring rate on the average particle diameter d_n (number).

As shown in Table 1, the behavior of this system is consistent with the characteristics of the above mentioned group B: similar time employed in reaching the identity point and 50% of polymer yield.

Number, Sauter and weight final average particle diameters are shown in Table 2. As expected, the larger particle sizes are reached for the lower stirring rates. When the stirring energy is too large (600-700 rpm), a significant breakup of individual drops is produced and the observed final particle size is smaller.

As mentioned above, the main goal of this study was to obtain a copolymer with a suitable particle size distribution. The amount of dispersant agent and the stirring rate are the main factors governing the particle size distribution. The amount of dispersant that can be used for its medical application was fixed in a previous work [15]. Therefore, the stirring energy could be only varied in order to obtain particle with the desired size distribution and it seems reasonable to seek a mathematical relationship between the final mean diameter and the stirring rate.

Hopff, et al. [18] derived by means of dimensional analysis the following simplified equation in the case of a suspension bead polymerization of the first group

TABLE 1. Time course of polymerization of MMA with STY.

| Time (min) | 400 rpm | | 450 rpm | | 500 rpm | | 600 rpm | |
|------------|---------------|-------------------------|---------------|-------------------------|---------------|-------------------------|---------------|-------------------------|
| | Pol.yield (%) | d_n (μm) | Pol.yield (%) | d_n (μm) | Pol.yield (%) | d_n (μm) | Pol.yield (%) | d_n (μm) |
| 60 | 11.16 | 14.80 | 11.90 | 13.83 | 13.05 | 12.10 | 11.27 | 12.57 |
| 120 | 24.11 | 32.01 | 25.12 | 28.55 | 23.94 | 20.43 | 24.27 | 16.41 |
| 150 | 37.63 | 42.02 | 40.78 | 31.83 | 35.90 | 27.39 | 35.40 | 19.77 |
| 180 | 65.21 | 44.67 | 62.54 | 33.35 | 65.72 | 29.76 | 66.61 | 21.88 |
| 210 | 67.52 | 45.06 | 72.39 | 33.18 | 72.56 | 31.60 | 67.40 | 21.82 |
| 270 | 68.31 | 45.34 | 73.21 | 33.92 | 73.88 | 31.64 | 67.84 | 22.04 |
| 400 | 70.26 | 45.20 | 73.21 | 33.96 | 75.00 | 31.72 | 68.02 | 21.96 |

TABLE 2. Influence of Agitation Rate on the Final Average Particle Size.

| Ag. rate (rpm) | d_n (μm) | d_{32} (μm) | d_w (μm) |
|----------------|-------------------------|----------------------------|-------------------------|
| 400 | 45.20 | 61.77 | 75.60 |
| 450 | 33.96 | 53.99 | 66.48 |
| 500 | 31.72 | 49.90 | 60.79 |
| 600 | 21.82 | 34.69 | 42.74 |
| 700 | 19.96 | 29.69 | 33.94 |

$$d_w = K N^{-1.5} \quad [2]$$

where N is the stirrer velocity (s^{-1}) and K a numerical constant.

Figure 4 shows the excellent fit between the experimental values and a straight line of slope -1.5. It means that a stirrer speed of 545 rpm would provide the desired particle size distribution in our experimental apparatus.

Figure 5 shows particle size distribution versus time for 400 and 600 rpm, respectively. It can be seen, for the slower stirring rate, that the mean value of particle size increases with time, undergoing from a unimodal distribution at the beginning of the experiment to a bimodal distribution as time progresses, with a high percentage of small particles. For higher stirring rates, the evolution of particle

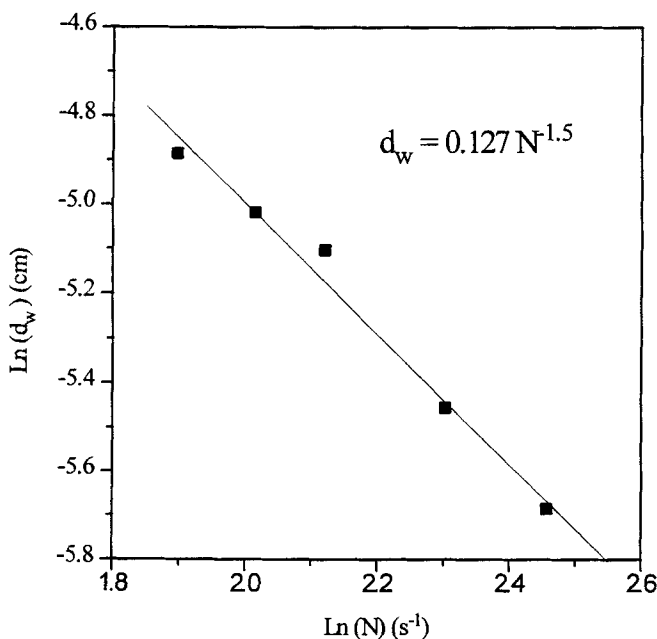


Figure 4. Dependence of the average particle diameter d_w (weight) on the stirring rate in the suspension copolymerization of methyl methacrylate and styrene.

size is less pronounced. Unimodal distribution remains along the run, rising only slightly the mean particle size during the experiment.

These findings are in agreement with those reported by other authors [19, 20].

The dispersant offers an enhanced protection of the smaller droplets, making more difficult the coalescence of two small particles than the coalescence of the greater ones. The concentration of dispersant determines the maximum particle surface area that can be stabilized and influences the interfacial tension. Increasing the concentration of dispersant leads to a decrease in particle diameter, as does lowering the interfacial tension [4].

Figure 6 shows the experimental conversion data obtained for the different runs. Curves shapes are consistent with a free radical polymerization reaction.

On the other hand, experimental results seem to be not affected by the stirring rate. It means that the reaction rate is not mass transfer controlled. As expected, our system exhibits the typical behavior of a suspension polymerization. Each bead

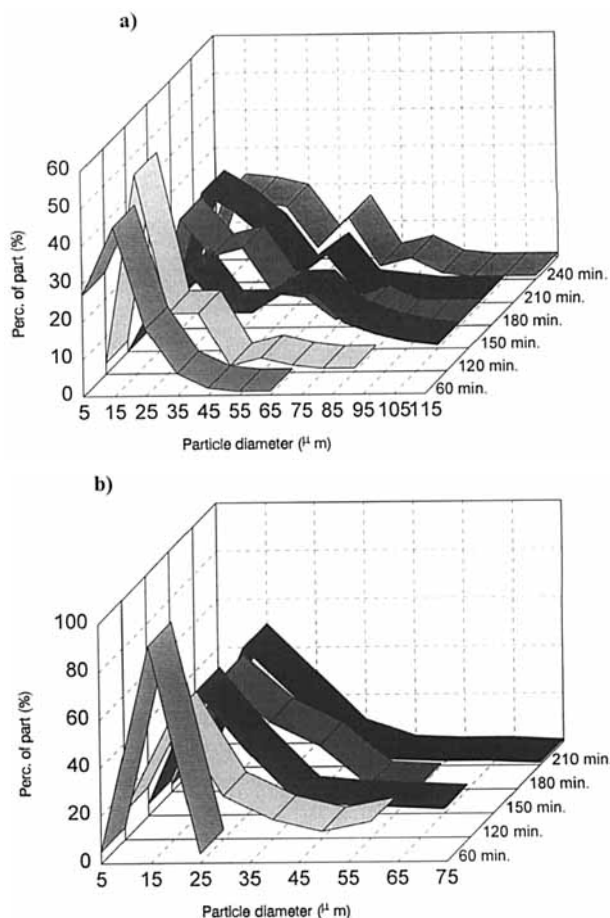


Figure 5. Particle size distributions at different reaction times for two different stirring rates. a) 400 rpm, b) 600 rpm.

may be regarded as a small isolated reactor and the observed copolymerization kinetic corresponds directly to that for bulk polymerization.

Finally, $^1\text{H NMR}$ spectra and GPC chromatography of the copolymer allow us to determine its composition and molecular weight, respectively. The analytical data, shown in Table 3, indicates that the composition of the copolymer is similar to the feed, due to the similar reactivity ratios of both monomers in the conditions of the experiment ($r_{\text{STY}} = 0.52$ and $r_{\text{MMA}} = 0.46$). The average molecular weight and the polydispersity of copolymer is quite similar to those reported in bibliography for SMA copolymers obtained in similar conditions [21].

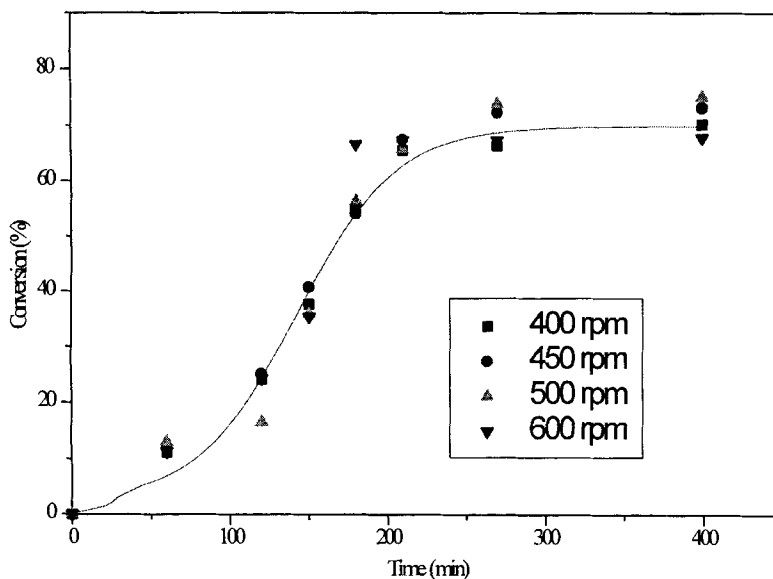


Figure 6. Suspension copolymerization of methyl methacrylate and styrene. Influence of stirring speed on the polymerization rate.

TABLE 3. Properties of the SMA Copolymer

| | |
|---|-----------------------|
| Mole fraction in the feed | 0.8 (MMA) 0.2(STY) |
| Mole fraction in the copolymer | 0.78 (MMA) 0.22 (STY) |
| Average molecular weight (weight) | 203338-212624 |
| Average molecular weight (number) | 82880-83370 |
| Polydispersity | 2.36-2.61 |
| Temperature of thermal degradation ($^{\circ}\text{C}$) | 405 ± 2 |

In Figure 7, the curve of thermal decomposition of the SMA copolymer is compared with that obtained from styrene and methyl methacrylate homopolymers. The characteristic temperatures at the beginning and end of rapid decomposition of SMA copolymer are quite similar to the MMA polymer [22]. The decomposition temperature of SMA (405°C) is higher than the decomposition temperature of polymethyl-methacrylate (386°C) but lower than the polystyrene (441°C). Thus, SMA copolymer exhibits an enhanced thermal resistance, compared with the majority monomer (MMA). It means that the addition of a relatively small quantity of styrene produces a significant increment of the polymer thermal resistance.

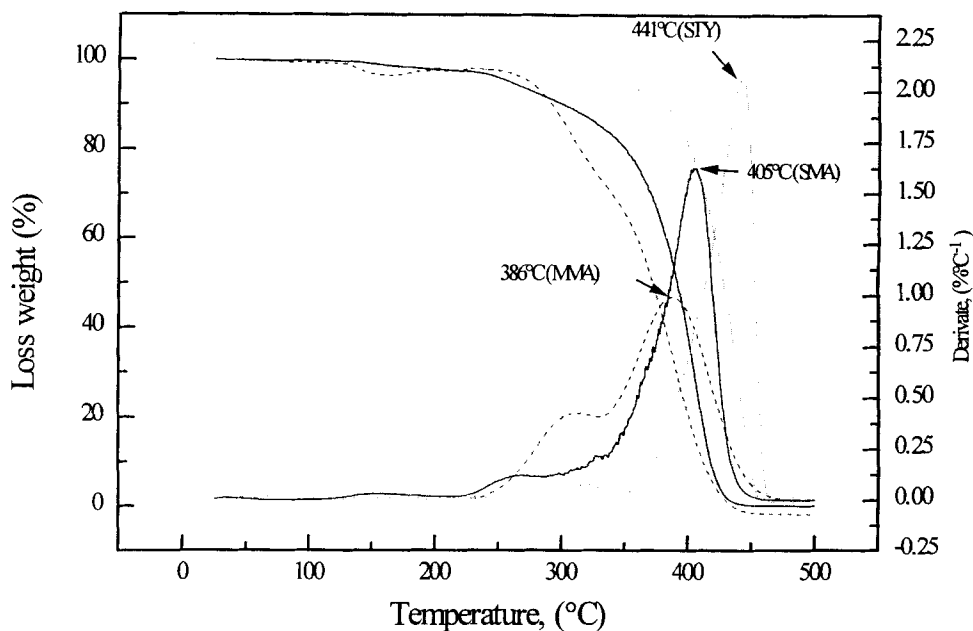


Figure 7. Thermogravimetric analysis of copolymer of methyl methacrylate and styrene, and the homopolymers of styrene and methyl methacrylate.

CONCLUSIONS

Suspension copolymerization of STY and MMA can be used to obtain a polymeric biomaterial with a suitable particle size distribution for its medical application. Although the identity point was reached after 30% of conversion, the final particle size could be related with stirring rate by a potential equation.

Polymer composition, molecular weight distribution and temperatures of thermal decomposition confirms that the SMA copolymer can be suitable for its medical application.

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Received November 20, 1996

Revision Received February 5, 1997