

# Modified Frontal Polymerization of Poly(methyl methacrylate)

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Received 21 May 2007; accepted 14 July 2008

DOI 10.1002/app.29358

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this work, we propose a modified frontal polymerization method to build a uniform reaction front by gradually immersing the reacting mixture in a thermal bath. This scheme allows uniform materials to be obtained with nearly constant molecular weights and polydispersities and a low residual monomer concentration. A comparative study of the molecular weight distributions of poly(methyl methacrylate)s obtained by bulk polymerization, frontal polymerization, and frontal polymerization with the proposed gradual immersion is presented. Samples obtained by these methods show that materials obtained by bulk polymerization and by frontal polymer-

ization are less uniform than those obtained by frontal polymerization with gradual immersion in a thermal bath. The obtained uniformity is directly related to a stabilizing effect of the reaction front by the gradual immersion of the reactor in a constant-temperature bath and to a reduction in the reaction rate promoted by a moderate transfer agent concentration. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1289–1295, 2010

**Key words:** degree of polymerization (DP); gel permeation chromatography (GPC); molecular weight distribution/molar; radical polymerization; synthesis

## INTRODUCTION

The synthesis of polymer materials with the same molecular weight distribution (MWD) at any point is a very important goal for many applications that require uniformity of physical or chemical properties. When a high optical transmittance over large regions is also required, as is the case in the production of polymeric optical fibers, the synthesis method becomes a great challenge because, in addition to the material uniformity requirements, a high optical transparency also requires high-purity materials.

Free-radical mass polymerization has become a preferred method for the production of optically

transparent materials to minimize contamination; however, the goal of a controlled synthesis is generally lost in such a system. Besides the unselective nature of radical reactions, a number of factors arising in the complex temperature and heat flow profiles that develop during such a polymerization become determinants of the local molecular properties of the synthesized materials. They generally become nonuniform.

The main problems in controlling the reaction parameters during polymerization arise from the characteristics of the gel-effect stage. Reduced heat diffusion combined with an increased reaction rate make the system locally unstable, creating small fluctuations amplified to a high enough degree to randomize the kinetics of the processes. Materials with diverse nonuniformities, from immersed bubbles to point-to-point variations of physical and chemical properties, are generally obtained.

During the last 4 decades, frontal polymerization (FP)<sup>1,2</sup> has emerged as a promising method for controlling free-radical polymerizations. The method is based on the propagation of a self-sustained reaction

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Contract grant sponsor: Consejo Nacional de Ciencia y Tecnología; contract grant numbers: 171820 (to A.G.V.), (to G.L.-B.), 58239 (through the Colaboración Interamericana de Materiales), and 78798.

front started at one of the system ends. As the front moves into the unreacted solution, a polymerized material is left behind. The system is stabilized because heat diffuses well into the reacting solution, and boundary conditions can be devised to build a stationary temperature profile that moves with the front. Variations include the type of initiator (thermal<sup>1-4</sup> or photoactive), the promoted temperature profiles, and the degree of chemical uniformity induced at the front. Compositional gradients,<sup>5</sup> designed to produce gradual variations of a desired property, have been obtained to offer the possibility of diverse functional materials. Very highly cross-linked materials<sup>6</sup> have also been prepared by FP, and potential applications are still under study.

Although FP studies started with poly(methyl methacrylate) (PMMA),<sup>1</sup> the interest soon moved toward systems with higher boiling temperatures because stabilization of the PMMA reacting front requires high pressures. Some research, using FP or other techniques, has been conducted on the production of optical-grade materials,<sup>7-16</sup> but no studies have been reported on the uniformity of frontally polymerized PMMA materials. As mentioned previously, such studies are important to support a number of applications and from a fundamental viewpoint.

In standard FP, the reaction front is started at one end of the system and self-propagates through the reacting solution, which commonly consists of the monomer and an initiator. To stabilize the process, delicate balances in the energy flows must be attained. Very often, front accelerations or decelerations are obtained because balances are lost, the system gets out of control, and nonuniformities arise in the synthesized materials.

To overcome such problems, we modified this procedure by introducing the reacting solution into a warming bath at a speed over the natural front velocity in an FP system, thus promoting an increase in the reaction speed while still keeping a constant temperature profile around the front. To identify and understand the parameters that control the process, we present in this work a comparison of the physicochemical characteristics of materials obtained by this method and materials obtained by standard bulk polymerization (SBP) and FP.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA; 99.95%), inhibited with 5 ppm 2,4,5-Trihydroxyphenyl alamine and obtained from Plastiglas (Lerma, Mexico) was dried with a molecular sieve until the water content, determined by the Carl Fisher method, was below 0.02%. The

inhibitor was then removed by high-vacuum distillation at 60°C. The purity was evaluated by gas chromatography to be better than 99.98% before the polymerization procedures.

*n*-Dodecyl mercaptan (DDM) from Sigma-Aldrich (St. Louis, MO) was also purified by vacuum distillation. The purity, also evaluated by gas chromatography, was better than 99.50%.

Lauroyl peroxide (LP; 99.95%) from Akzo-Nobel (Amsterdam, Netherlands) was used as received, but the concentration of active oxygen was 4% as determined by iodimetry.

Helium (99.99%) from Grupo Infra (Queretaro, Mexico) was used as a sweeping gas to remove dissolved gases in the prepared reaction mixtures.

All reactions were carried out in borosilicate glass tubes washed with neutral soap, immersed in nitric acid (5%) with distilled water, and rinsed with deionized water.

### Experimental procedure

A set of samples made from the same batches of reactants were prepared within a class 10,000 clean room in the following way. Mixtures of MMA with  $4.7 \times 10^{-3}M$  LP as the initiator and variable proportions of the transfer agent (DDM; from 0 to  $2.36 \times 10^{-2}M$ ) were stirred and passed through an inorganic filter (0.1- $\mu m$  membrane, Millipore (Billerica, MA)) to obtain a homogeneous polymerization solution. The solution was then poured into the glass tube reactors up to roughly 80% of their capacities, and helium was bubbled for 30 min to sweep dissolved oxygen. The tubes were then immediately sealed with polytetrafluoroethylene stoppers.

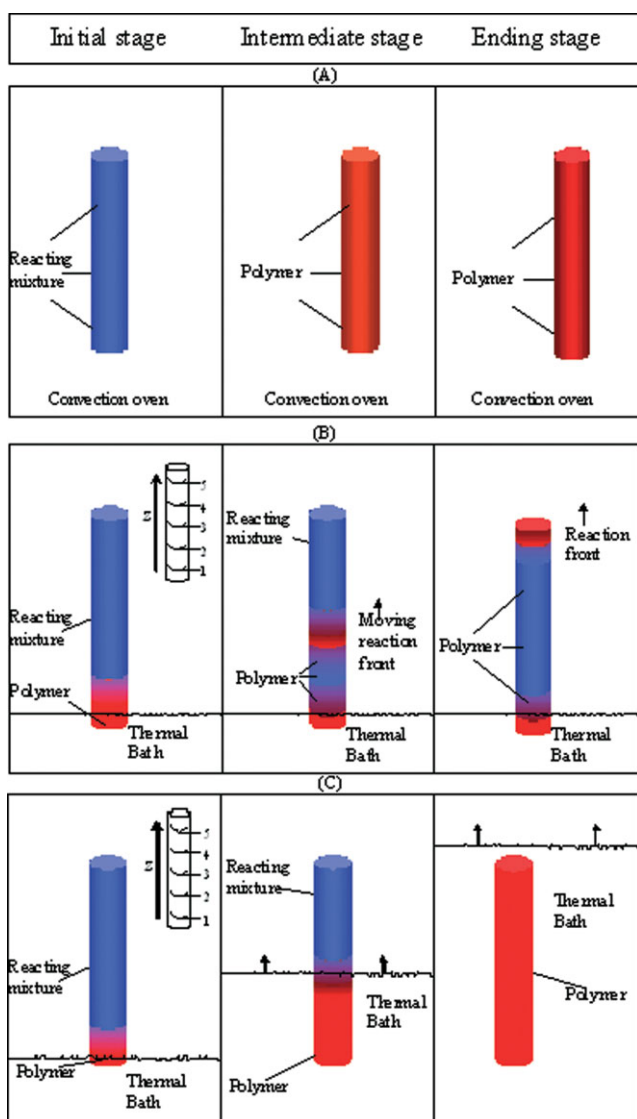
The prepared reaction mixtures (at least three per run) were then subjected to one of the following procedures. A general scheme of the reaction procedures can be seen in Figure 1.

### SBP

Reactors were placed into a forced convection oven at 50°C for 44 h, which produced a 97% degree of conversion. Under these conditions, the polymerization passed through a medium degree of conversion stage characterized by a moderate gel effect.

### FP

The bottom of the reactor, containing 7% of the reacting mixture, was introduced into a mineral oil thermal bath at 50°C, whereas the room temperature was held at 25°C. The sample polymerization started from the bottom of the reactor, and a propagating front developed that moved toward the top of the reactor. Samples with 0, 0.00254, and 0.011M transfer agent concentrations (TACs) were obtained by this



**Figure 1** General scheme for the polymerization processes studied in this work. (A) SBP: Reactors with a reacting mixture (monomer, initiator, and transfer agent) are placed in a forced convection oven with a uniform temperature. (B) FP: The lower end of the reactor is introduced into a thermal bath to produce a rising reaction front. (C) FPGI: The reactor is introduced at a low position within the thermal bath to keep the reaction front slightly below the bath level. For both FP and FPGI processes, the temperature is monitored at each of the five points depicted in the insets. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

method. For higher TACs, the polymerization times greatly increased.

#### Frontal polymerization with gradual immersion (FPGI)

The bottom of the reactor, containing 7% of the reacting mixture, was introduced into a mineral oil thermal bath at 50°C. The immersion process started 2 h before the development of the polymerization

front. This front was evidenced by a temperature rise in the first temperature sensing point (see Fig. 1). The reactor was immersed at a constant immersion speed until the bath completely covered the reacting mixture.

The immersion speed was set to 80% of the natural polymerization front speed for the FP process at each TAC. Such a speed was shown to be an adequate experimental selection between the extreme operating scenarios, both promoting adverse unwanted effects. For lower immersion speeds, the polymerization front tended to escape from the warming thermal bath surface, an increasing advance of the polymerization front with respect to the thermal bath surface developed, and the polymerization process became similar to that of the FP method; besides, there was an unwanted increase in the overall reaction time. On the other hand, at higher immersion speeds, because the reacting mixture was immersed as a whole within the uniform temperature environment of the thermal bath, the polymerization conditions became similar to those of the BP method. In such a case, the gel effect occurred uniformly in the whole reacting mixture. For the highest immersion speeds, the obtained materials resembled those obtained by the BP process.

In all the procedures, the final step consisted of increasing the temperature of the reactor tubes to 120°C (slightly above PMMA's glass-transition temperature) in the oven used for the SBP procedure. This temperature was held for 3 h, after which the system was cooled to 50°C in 2 h. In all cases, the temperature was maintained within  $\pm 0.5^\circ\text{C}$  of the set point.

#### Measurements

For FP and FPGI, the temperature of the outer reactor wall was monitored at five points separated by 20% of the final length of the polymerized bar (see the inset in Fig. 1). For this purpose and because there was a volume contraction from the initially liquid mixture to the solid polymerized bar, a series of preliminary test runs were carried out to determine the final length of the polymer bar.

Trials to measure the reaction mixture temperature with available thermocouples proved to be troublesome because, besides introducing material contamination, measuring probes promoted bubble formation that modified the temperature profiles and increased the measurement fluctuations, making temperature readings unreliable and misleading. We decided to adhere to the observations made by Evstratova et al.,<sup>17</sup> according to which the temperature just outside the reactor gives a rough indication of the reaction temperature within the tubes. Therefore, although measured temperatures are only

**TABLE I**  
 $M_w$ , PD, and RM Values and Their Corresponding Standard Deviations ( $\sigma M_w$ ,  $\sigma$ PD, and  $\sigma$ RM) for Samples Prepared with the SBP Procedure

TAC ( $\times 10^{-3}M$ )	$M_w$ ( $\times 10^3$ )	$(\sigma M_w)/M_w$ (%)	PD	$\sigma$ PD	RM (%)	$\sigma$ RM
0.00	3000	32	7.9	1.2	0.7	1.3
2.54	420	24	6.4	0.22	0.7	1.1
11.00	285	14	2.5	0.19	0.7	0.7
12.70	219	12	1.9	0.20	0.7	0.3
14.10	168	11	1.8	0.15	0.7	0.3
16.00	132	11	1.8	0.111	0.6	0.2
23.60	107	10	1.7	0.16	0.6	0.2

indicative of the local conditions, this procedure keeps the reacting solution unperturbed, and observations become meaningful.

Once the polymerization was completed, the glass reactors were broken to get the synthesized materials out. Five slices were cut at regular intervals along the obtained bars. The sample slices were crushed and dissolved in filtered high-performance liquid chromatography grade tetrahydrofuran from Aldrich to obtain their MWD by size exclusion chromatography in a PerkinElmer (Waltham, MA) high-performance liquid chromatograph. Small parts of the crushed materials were also dissolved in reactive-grade toluene to determine their residual monomer concentrations (RMs) by gas chromatography in a Hewlett-Packard (Ramsey, MN) gas chromatograph.

## RESULTS AND DISCUSSION

Tables I–III present the weight-average molecular weight ( $M_w$ ), average polydispersity (PD), and RM values as well as the corresponding standard deviations of these parameters ( $\sigma M_w$ ,  $\sigma$ PD, and  $\sigma$ RM, respectively) as function of the TAC for each set of samples prepared by each of the described methods. Such averages were calculated from the corresponding parameters for each MWD curve obtained for the five zones in each polymerized bar over a minimum of three bars.

It is clear from the reported data that material uniformity, evaluated by  $\sigma M_w$  and  $\sigma$ PD along and through the obtained samples, is strongly influenced by the TAC value and the polymerization method. The most uniform materials were obtained by the FPGI method at moderate TACs (from 0.011 to 0.016M), whereas lesser uniformity is associated with the SBP method and the lower TACs (from 0.0 to 0.00254M). Figure 2 shows the molecular weight measurements of the five polymer discs taken from the bar.  $M_w$  variations along the bars diminish from the SBP materials to the FP materials to the FPGI materials, suggesting more stable reaction conditions.

Typical bulk polymerizations produce materials with occluded bubbles, which are highly undesir-

able. Larger polymer nonuniformities are correlated with higher bubble incidence within the synthesized material. Because bubbles can also be associated with larger temperature fluctuations during the gel effect stage, it is natural to link nonuniformities of mass-polymerized materials to the complex temperature distribution and energy flow arising during the gel effect stage of the process.

Results shown in Tables I–III and Figure 2 suggest that moderately slow FP promotes a local stabilization of the process. Note that molecular weight variations are diminished from SBP to FP to FPGI. Tables I–III show that the characteristic parameters related to material uniformity,  $\sigma M_w/M_w$  (%), PD,  $\sigma$ PD, RM (%), and  $\sigma$ RM, also diminish in a similar fashion.

As claimed in general for other types of FP processes, such stabilization seems to be a result of the higher diffusional parameters in the low viscosity liquid than in the high viscosity liquid produced because of the gel effect; however, we have also found a stabilizing effect due to a retarding effect in the polymerization introduced by the transfer agent. The used transfer agent promotes a reduction in the rate of heat generation and a corresponding softening of the gel effect in the reaction.

It has been reported that a transfer agent, specifically DDM, causes retardation of the onset of the gel effect in MMA polymerization and that the autoacceleration due to the gel effect becomes less pronounced as the concentration of the chain-transfer agent is increased.<sup>18</sup> This can be explained in terms of the well-known polymerization rate expression for free-radical polymerization:<sup>19</sup>

**TABLE II**  
 $M_w$ , PD, and RM Values and Their Corresponding Standard Deviations ( $\sigma M_w$ ,  $\sigma$ PD, and  $\sigma$ RM) for Samples Prepared with the FP Procedure

TAC ( $\times 10^{-3}M$ )	$M_w$ ( $\times 10^3$ )	$\sigma M_w/M_w$ (%)	PD	$\sigma$ PD	RM (%)	$\sigma$ RM
0.00	3010	25	4.5	2.4	15.1	5.7
2.54	521	12	2.6	0.15	14.8	5.7
11.00	129	6	2.3	0.13	13.9	6.6



**TABLE III**  
 $M_w$ , PD, and RM Values and Their Corresponding Standard Deviations ( $\sigma M_w$ ,  $\sigma PD$ , and  $\sigma RM$ ) for Samples Prepared with the FPGI Procedure

TAC ( $\times 10^{-3}M$ )	$M_w$ ( $\times 10^3$ )	$(\sigma M_w)/M_w$ (%)	PD	$\sigma PD$	RM (%)	$\sigma RM$
0.00	3100	6.0	2.9	0.19	0.7	0.10
2.54	407	5.1	2.7	0.15	0.7	0.05
11.00	134	3.6	2.2	0.06	0.7	0.02
12.70	132	2.8	2.0	0.05	0.6	0.02
14.10	111	3.3	2.2	0.09	0.6	0.02
16.00	106	2.3	2.2	0.07	0.6	0.02
23.60	75	5.4	2.2	0.08	0.6	0.01

$$R_p = k_p[M] \left( \frac{fk_d[I]}{k_t} \right)^{1/2} \quad (1)$$

where  $R_p$  is the rate of polymerization (M/s);  $k_d$ ,  $k_p$ , and  $k_t$  are the kinetic coefficients for the initiator decomposition ( $s^{-1}$ ), propagation step ( $M^{-1} s^{-1}$ ), and bimolecular termination ( $M^{-1} s^{-1}$ ), respectively;  $f$  is the initiator efficiency; and  $[M]$  and  $[I]$  are the monomer and initiator molar concentrations, respectively. Here  $k_t$  is an effective value that includes diffusion limitations and decreases by even orders of magnitude during the gel effect stage, so the rate of polymerization increases significantly (autoacceleration) at the onset of the gel effect. In the presence of DDM and because of the lower molecular weights produced in the presence of the transfer agent, the diffusion limitations associated with the restricted mobility of the long chains are less severe, and  $k_t$  decreases, but moderately, retarding the autoacceleration and making it milder. It is important to note that this rate retardation is not due to a slow reinitiation of the TAC radical, as it has been reported that before the onset of the gel effect or in solution, the presence of DDM does not affect the polymerization rate.<sup>18,20</sup> The temperature profiles obtained for the FP process, shown in Figure 3, give an idea of the way in which heat is generated around the polymerization front for different TAC values. Although profiles for TAC values of only 0 and 0.00254M are presented, it is clear that the width and height of the temperature peaks associated with the polymerization front change dramatically from the case with no transfer agent to the case with it. It is noteworthy that the addition of a transfer agent promotes a significant decrease in the peak-to-base temperature changes ( $\Delta T = T_{\text{peak}} - T_{\text{base}}$ , where  $T_{\text{peak}}$  is the peak temperature and  $T_{\text{base}}$  is the base temperature) from  $\Delta T \sim 50^\circ\text{C}$  (0.0M TAC) to  $\Delta T \sim 5^\circ\text{C}$  (0.00254M TAC).

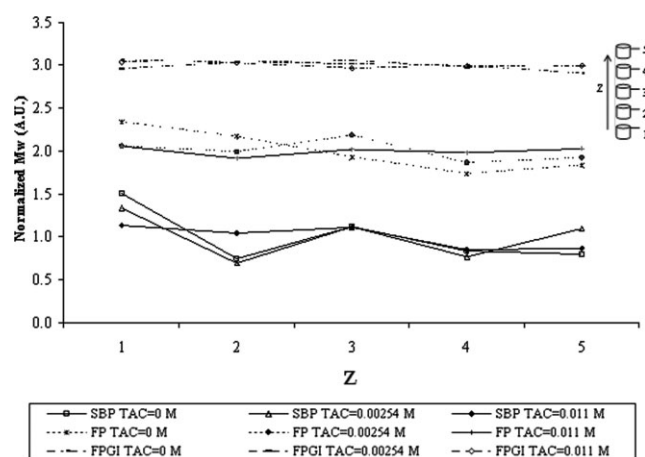
The heat production for the FP without a transfer agent is high enough to promote a self-propagating front, which in fact accelerates, showing a tendency to become unstable. Temperature gradients exist within the whole reaction mixture; however, large

values are concentrated around the polymerization front, making convection a determinant factor of the local reaction conditions.

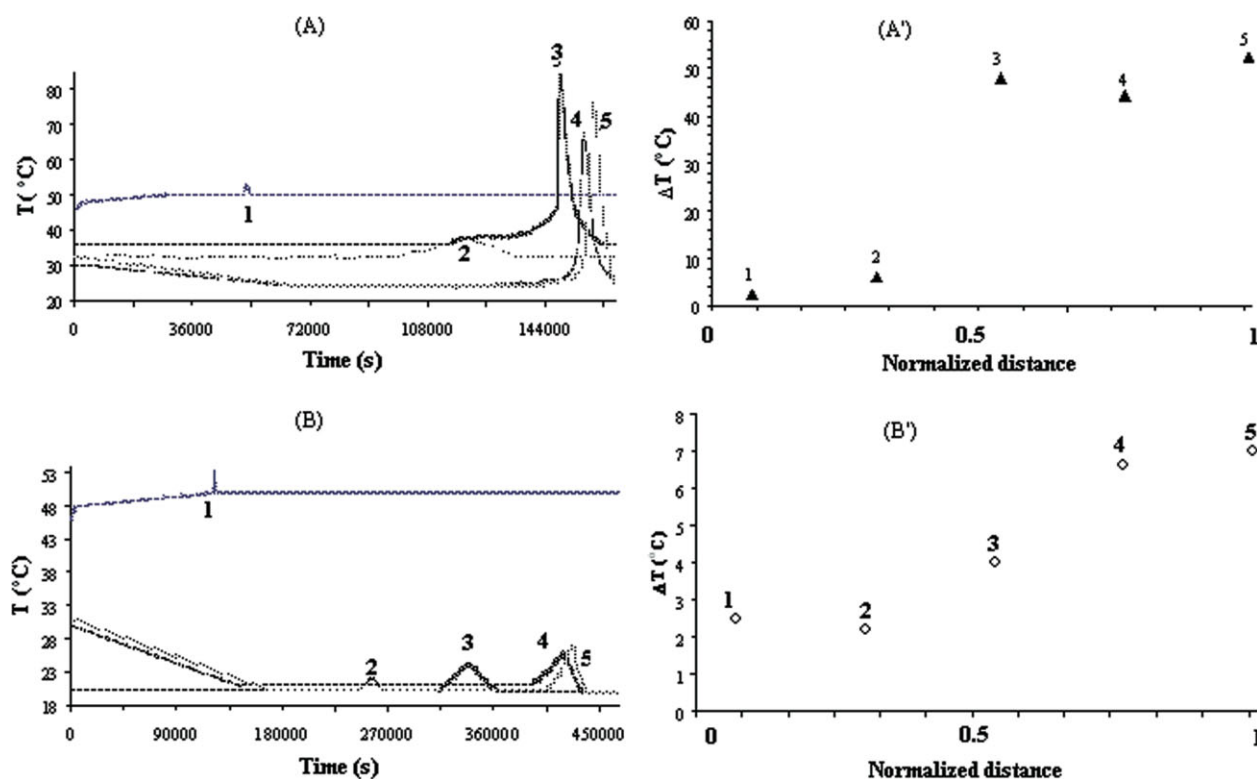
For the case with a 0.00254M TAC, temperature profiles show comparatively smaller peaks, and the polymerization front velocity and acceleration are comparatively reduced. Diminished heat flow and convection are expected in this case.

Table IV shows the  $M_w$ , PD, and RM values for the corresponding FP samples. The larger uniformity of the sample with the transfer agent is clear, as shown by the low and uniform PD values.

The aforementioned retarding effect introduced by the transfer agent is clear from the lower average front velocity obtained for the sample with the transfer agent. Figure 4 shows such a speed for the three tested TAC values and the extrapolated values for other concentrations. Note that when the TAC increases from 0.00254 to 0.011 (a factor of 4), there is a decrease of almost 2 orders of magnitude in the reaction front speed. Consequently, a larger TAC becomes unpractical for the studied conditions.



**Figure 2** Comparison of normalized values for  $M_w$  along the PMMA bar obtained with three polymerization techniques (SBP, FP, and FPGI) and different TACs (0, 0.00254, and 0.011M). The values are normalized, and those for FP and FPGI processes are displaced by 1 and 2 units to visualize  $M_w$  variations for each polymerization technique.



**Figure 3** FP temperature profiles measured at the reactor tube wall for samples with TACs of (A) 0 and (B) 0.00254M. The  $\Delta T$  values observed at each position are shown in (A',B') graphs for TACs of 0 and 0.00254M. Thermometer positions 1–5 are uniformly separated (by roughly 20%) as depicted in Figure 2. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Conversely, a transfer agent offers a more controlled reaction, as discussed before. The FPGI process partially compensates for the retarding effect by gradually matching the polymerization front with the liquid thermal bath level. This allows a uniform reaction front by maintaining the polymerization within a narrow region.

By comparing Tables I–III, we note that FPGI works better than both SBP and FP because the normalized  $\sigma M_w$ ,  $\sigma PD$ , and  $\sigma RM$  values are smaller for all TAC cases. Our modified FPGI takes advantage of immersing the reacting mixture to stabilize the reaction front and the whole polymerization system.

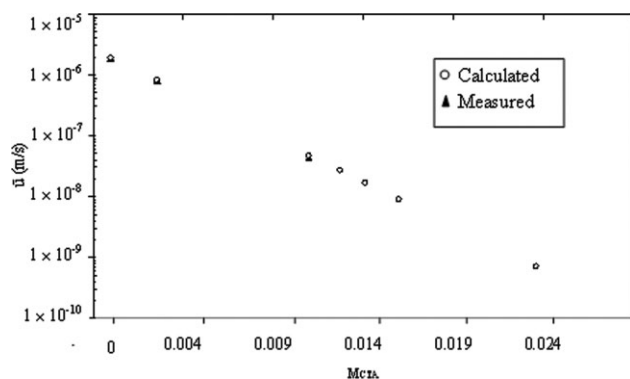
For lower TAC values, the immersion-induced acceleration of the front is not enough to move the FP process into a stabilized one, and for the largest TAC values, corresponding to very slow polymerization fronts, the immersion is not enough to accelerate the reaction rate significantly, so the process is driven into the SBP regimes.

From Tables II and III, it is noteworthy that our proposed FPGI method allows better control of the polymerization front in comparison with the FP method. A comparison of the PD values for the same TAC values (from 2.54 to  $23.6 \times 10^{-3}M$ ) for all three methods shows a systematic decrease in  $\sigma M_w$ ,

**TABLE IV**  
*M<sub>w</sub>*, PD, and RM Values at Different Positions in an FP Sample

Position	TAC (M)					
	0.0			$2.54 \times 10^{-3}$		
	<i>M<sub>w</sub></i> ( $\times 10^3$ )	PD	RM (%)	<i>M<sub>w</sub></i> ( $\times 10^3$ )	PD	RM (%)
1	4021	2.3	5.0	549	2.4	4.8
2	3508	2.3	17.2	515	2.5	16.2
3	2806	4.0	18.0	615	2.7	17.0
4	2203	6.6	18.2	451	2.7	18.2
5	2512	7.4	17.3	479	2.8	17.9
<i>u</i> (m/s)	$1.88 \times 10^{-6}$			$8.05 \times 10^{-7}$		

The average velocity of the polymerization front (*u*) is given for both TAC values.



**Figure 4** Polymerization front velocity ( $u$ ) as a function of TAC for the FP process. Measured values correspond to samples actually prepared, whereas calculated values were obtained from them by simple logarithmic fitting.

PD, and  $\sigma$ PD from FPGI to FP to SBP ( $\sigma_{\text{FPGI}} < \sigma_{\text{FP}} < \sigma_{\text{SBP}}$ ). These observations are mainly due to a more uniform reaction temperature profile from FPGI to FP to SBP, as suggested by modeling studies of FP processes.<sup>21,22</sup>

As suggested by Figure 3, in the FP process, each point within the material is polymerized by a wavy-type reaction process,<sup>17</sup> in which a relatively low reaction temperature is set and maintained in every section of the material until the reaction front arrives at it and raises the temperature for some time to finally decay approximately to room temperature (see Fig. 1). In the case of the SBP and FPGI processes, the temperature of the surrounding environment presumably holds the reaction mixture at higher temperatures for longer times. Note that the environment for the SBP process is the controlled convection oven itself, and for the FPGI process, the thermal bath eventually covers the reactor completely. A local temperature rise for each section in the material leads to the highest reaction rate in the zone [ $R_p$  in eq. (1)], so the much larger RMs observed for the FP process seem to be a result of the shorter times that the reaction is held at high temperatures in comparison with the SBP and FPGI processes. The higher temperature stage, in which the polymerized bar is heated to 120°C (see the Experimental section), is clearly insufficient to complete the polymerization to a high degree of conversion.

As shown in Table IV, smaller RM concentrations were observed at the bottom of the FP bars (position 1) than at the remaining positions (2–5). Tables I and III also show that for the lower TAC,  $\sigma_{\text{RM}}$  for the FPGI samples was also smaller than for the SBP ones. This might be a result of better efficiency in

the initiation reaction under the milder heating conditions of the FPGI process.

## CONCLUSIONS

A comparative study of PMMA mass-polymerized by SBP, FP, and FPGI has shown that highly uniform materials can be obtained by FPGI at moderate TACs (0.00254 and 0.011M). FPGI takes advantage of building a more localized, narrow polymerization front, which develops in the FP process, with the benefit of controlling the movement of this front by gradual immersion of the reactor in a thermal bath. The addition of a transfer agent helps to stabilize the reaction front by slowing down the reaction rate and the corresponding heat generation in the polymerization front.

The proposed FPGI process allows the development of steady-state reaction conditions by forcing the formation of a paced reaction front. These conditions are not easily achieved in a typical FP process.

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