

# Expandable Styrene/Methyl Methacrylate Copolymer: Synthesis and Determination of VOCs by Combined Thermogravimetry/Differential Thermal Analysis-Gas Chromatography/Mass Spectrometry

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Received 30 April 2011; accepted 22 August 2011

DOI 10.1002/app.35513

Published online 6 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Parts cast of metals using expandable polystyrene foams may have an unacceptable amount of surface defects, such as lustrous carbon. The use of foams made of styrenic/acrylic copolymers can improve the quality of foam molds and metal parts made using such molds. Lost foam copolymer was synthesized by suspension copolymerization of styrene and methyl methacrylate. The polymerization was carried out in the presence of blowing agents. The decomposition products of lost foam beads were studied by a method composed of the thermogravimetry/differential thermal analysis (TG/DTA) and gas chromatography/mass spectrometry (GC/MS). With these systems, the TG/DTA data can be combined with a GC separation and MS identi-

fication methods. This combined method improves the analysis of the decomposition products of lost foam beads and enables the precise identification of the amount and the nature of volatile organic compounds (VOCs) trapped during suspension polymerization. The results obtained from the combined method were verified for the nature and amount of VOCs with the results of time-conversion studies for copolymerization of monomers in the presence of different concentrations of blowing agent. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4711–4720, 2012

**Key words:** suspension polymerization; expandable copolymer; blowing agent; TG/DTA-GC/MS analysis

## INTRODUCTION

Styrenic polymers have a wide variety of applications, including the formation of expandable polystyrene (EPS) particles, which can be used to make a variety of products. Processes for forming styrenic polymer particles include emulsion polymerization, suspension polymerization with accompany of particular suspensions or emulsion aids. EPS foams and other expanded resins can be prepared from expandable polymeric particles made by contacting the polymeric beads with a volatile compound known as a “blowing agent” or “expanding agent.” Such agents include aliphatic hydrocarbons such as butane, pentanes, hexanes, and halogenated hydrocarbons such as trichloromethane, trichlorofluoromethane, and methyl chloride.<sup>1–12</sup> The particles in contact with the expanding agent may be expanded by heating or by exposure to reduced pressure as in a vacuum. The size and size distribution of the ex-

pandable particles (compact particles) influence the size and size distribution of the particles after expansion.

Both the expanded and expandable polymers have applications in packaging, consumer products, and in materials processing. Examples of materials' processing applications for expanded polymers include so-called lost foam or evaporating pattern casting (EPC). In lost foam casting, a molten metal is poured into a pattern made of expanded polymeric material, that is, foam coated with a refractory material surrounded and supported by unbounded sand. The foam is decomposed by the heat of the molten metal and replaced by the metal.<sup>13–16</sup>

In recent years, an EPC technology is increasingly used in casting technology, which is a new technique without residuals and with excellent molding accuracy. In this method, a readily volatilizable foam is used as mold pattern and it is unnecessary to take out the mold. Therefore, any mold joint and any sand core are eliminated. The dimensional accuracy and the surface roughness of the metal parts produced by this method are comparable with the ones in the investment casting.<sup>17,18</sup> Because of possibility of carbon pickup, the process using EPS patterns is

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not suitable for black metal casting since the carbon-rich benzene structure produced during degradation of EPS is thermodynamically stable and difficult to be decomposed. Furthermore, the EPS decomposition leads to a plenty of liquid, which is contacted with molten metal for a long time, making carbon-hydrogen bond of benzene ring structure be cracked to form carbon residual and therefore increasing the possibility of carbon being captured by liquid metal in mold. In summary, the EPS mold has a main disadvantage of carbon pickup defect in casting. The use of foams made of styrenic/acrylic copolymers can improve the quality of foam molds and metal parts made using such molds.<sup>19</sup>

Traditional manufacturing of expandable resins in bead form involves two different processes. First, free radical aqueous suspension polymerization of monomer (monomers) is carried out at temperature between 80 and 90°C with the aid of monofunctional initiators, such as azobisisobutyronitrile or benzoyl peroxide (BPO).<sup>20</sup> The second process, called the impregnation stage, consists of a high temperature-high pressure cycle in which the blowing agent, commonly *n*-pentane, is loaded in the reactor and diffuses into the softened beads.<sup>21</sup> As the free radical polymerization reactions rarely proceed to completion, leading to the presence of unreacted residual monomer in the polymeric material, knowledge about the content of volatile residual monomers, blowing agent, and impurities and additives in such plastics is important in special application such as EPC.

Volatile organic compounds (VOCs) "off-gassing" and other airborne particles, which could be carcinogenic, fill our lungs every day. Many of these VOCs come from polymeric foam such as expandable polystyrene (EPS) and cellular polyethylene foams used all around buildings, even insulation, packaging, vibration damping, and founding industry. Eliminating or even control and minimizing as many of these harmful chemicals as possible can not only help the quality of our designs but also boost the environmental aspects of beings life. The bead expansion/molding process uses steam and break down into harmful byproduct of blowing agents and trace amounts constituting monomers dissipates shortly after molding. Besides affecting pattern and ultimately mold bulk and surface properties, residual monomers and blowing agents are often toxic and may affect the quality of products stored inside in the packaging of the food, beverages, cosmetic, or medicines.

Commercial EPS typically contains 7–8 wt % of pentane isomers (mainly *n*-pentane and *i*-pentane) as physical blowing agents.<sup>1</sup> This blowing agent is capable of expanding the compact polystyrene (PS) beads on heating the material above its glass transition temperature ( $T_g$ ). The vapor pressure of

the blowing agent forces the softened PS matrix to expand and a homogeneous cellular structure with irregular polyhedral-shaped closed cells is formed.

Some essential differences in expansion behavior can be expected for lost foam with respect to conventional EPS. Besides the nature of the physical blowing agent and the expansion conditions (temperature, pressure, and heating medium), the expansion characteristics of lost foam beads are strongly influenced by the properties of the polymer matrix.<sup>18</sup> The presence of methyl methacrylate (MMA) monomer imposes some different properties in the lost foam matrix. Therefore, the properties of PS matrix in EPS are very different compared with St/MMA copolymer matrix in expandable St/MMA copolymer beads. During the expansion process, the viscoelastic properties of the matrix influence the foam stability and its expandability. On the other hand, a certain degree of melt strength or elasticity is required to prevent viscous flow failure of the cell walls and collapsing the foam.

Because of problems with the direct gas chromatographic (GC) analysis of a polymer solution, the organic emissions from plastics are usually controlled by various hyphenated GC techniques, for example, coupling of GC with headspace,<sup>22–25</sup> thermal desorption,<sup>26–28</sup> pyrolysis,<sup>29,30</sup> and more recently, solid phase microextraction.<sup>31–40</sup> In the first part of this work, we have presented the results from extensive studies of aqueous suspension copolymerization of styrene (St) and MMA in the presence of pentane as foaming agent using the optimized conditions obtain from previous work.<sup>17,18</sup> The second part is devoted to precise estimation of total blowing agent contents and residual monomer in the compact synthesized lost foam beads. The kinetic of decomposition and volatile release was obtained by thermogravimetry (TG), which has been used for a number of years in polymer chemistry.<sup>41</sup> Volatile products were analyzed by coupling thermogravimetric technique with GC and mass spectrometry (MS). Monomer conversion rate is one of the parameters used for evaluating the free radical suspension polymerization process. It can be obtained by the traditional method, typically, gravimetry. In this work, we used an ampoule polymerization technique for investigation of polymerization reaction progression and residual monomer level in the final copolymer product. In order to bring a new, rather industrial-oriented drive into the research on pilot scale polymerization, with a major focus on the suspension polymerization and the kinetic particularities connected to it, a comparison was made with copolymer products provided from industrial grade raw materials.

TABLE I  
Recipes for the Batch Suspension Polymerization Experiments<sup>a</sup>

Run	T (°C)	BPO <sup>b</sup> (wt %)	TCP <sup>b</sup> (wt %)	DBSNa <sup>b</sup> (wt %)	Pentane <sup>b</sup> (wt %)	PVA <sup>c</sup> (wt %)	PVP <sup>c</sup> (wt %)	HEC <sup>c</sup> (wt %)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> <sup>c</sup> (wt %)	DVB <sup>b</sup> (wt %)	PW <sup>b</sup> (wt %)	Stirring speed (rpm)
1	80	0.20	0.15	0.0017	0	0.05	0.1	0.32	0.0024	0.01	0.25	280
2	80	0.20	0.15	0.0017	5	0.05	0.1	0.32	0.0024	0.01	0.25	280
3	80	0.20	0.15	0.0017	10	0.05	0.1	0.32	0.0024	0.01	0.25	280
4	80	0.20	0.15	0.0017	15	0.05	0.1	0.32	0.0024	0.01	0.25	280

<sup>a</sup> Monomer hold-up: 40 vol %

<sup>b</sup> Based on organic phase.

<sup>c</sup> Based on aqueous phase.

## EXPERIMENTAL

### Materials

MMA and St monomers were washed twice with 5 wt % aqueous solution of sodium hydroxide followed by washing twice with distilled water to eliminate the inhibitor, radical initiator BPO (active content 75%, water 25%) with  $t_{1/2} = 75$  min at 90°C, the drop stabilizers poly(vinyl alcohol) (PVA) with a degree of hydrolysis of 72.5% and a molecular weight of 72,000 g/mol, hydroxyethyl cellulose (HEC), and poly(vinyl pyrrolidone) (PVP; 360,000 g/mol), divinyl benzene (DVB) as a crosslinker and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) as a aqueous phase initiator were supplied by Merck. Tricalcium phosphate (TCP) and sodium dodecylbenzenesulfonate (DBSNa) were supplied by Fluka and were used as received. Zinc stearate, pentane (35 wt % *n*-pentane and 65 wt % *i*-pentane) as blowing agent, and polyethylene wax (PW) as a cell structure modifying aid were supplied by Tabriz petrochemical company (TPC), Tabriz, Iran. Silicone oil (Therm 420) was supplied by Lauda and was used as received. All industrial grade raw materials were provided from TPC.

### Suspension polymerization of expandable poly(St-co-MMA)

Based on optimum polymerization conditions as discussed in the previous papers,<sup>17,18</sup> three main formulations were developed for the preparation of lost foam beads. The details of polymerization recipes are presented in Table I. The expandable St-MMA copolymer particles were synthesized by a batch suspension copolymerization. The required amount of PVA, TCP, PVP, HEC, DBSNa, and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were fed into the reactor containing preweighed amount of distilled deionized water. The mixture was kept stirred at ambient temperature under moderate stirring (280 rpm) for at least a few hours due to produce a homogeneous mixture. In order to control the final polymer particle size and size distribution, the reaction parameters including the concentrations of

stabilizer and suspending agents and the stirring speed used in the experiments were optimized using an experimental design procedure.<sup>17</sup> A monomer emulsion tank reactor was made by adding a mixture of St and MMA monomers (70 wt % MMA and 30 wt % St), free radical initiator (BPO), molecular weight modifying aid (DVB), and cell structure improver (PW). After this, the blowing agent containing mixed pentanes (35 wt % *n*-pentane and 65 wt % *i*-pentane) was fed into the emulsion tank. After the mixture was being stirred for 30 min, the content of monomer emulsion tank was transferred to the reactor. The reactor was sealed and purged with 5 psig nitrogen and repressurized to 5 psig nitrogen. When all of the reaction mixture had been added and after 30 min hold time, the reactor was heated to the reaction temperature (80°C) at a rate of 0.5°C/min and held for 7 h. In order to control the final blowing agent content in the expandable copolymer particles, we used a pressurized period created by nitrogen purging during the polymerization course. The details of the applied pressure effects on the final blowing agent content and the cell structure of the expanded particles will be published elsewhere. The reaction temperature profile and a typical utilized pressure cycle are illustrated in Figure 1. After the completion of the reaction, the reactor was cooled to 35°C at a rate of about 5°C/min. The reaction mixture was transferred to a batch out tank without washing residual material into the tank. The reaction mixture containing the expandable St-MMA

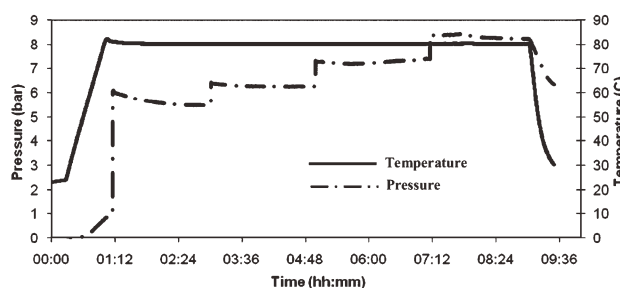


Figure 1 Typical temperature and pressure profile in the suspension copolymerization.

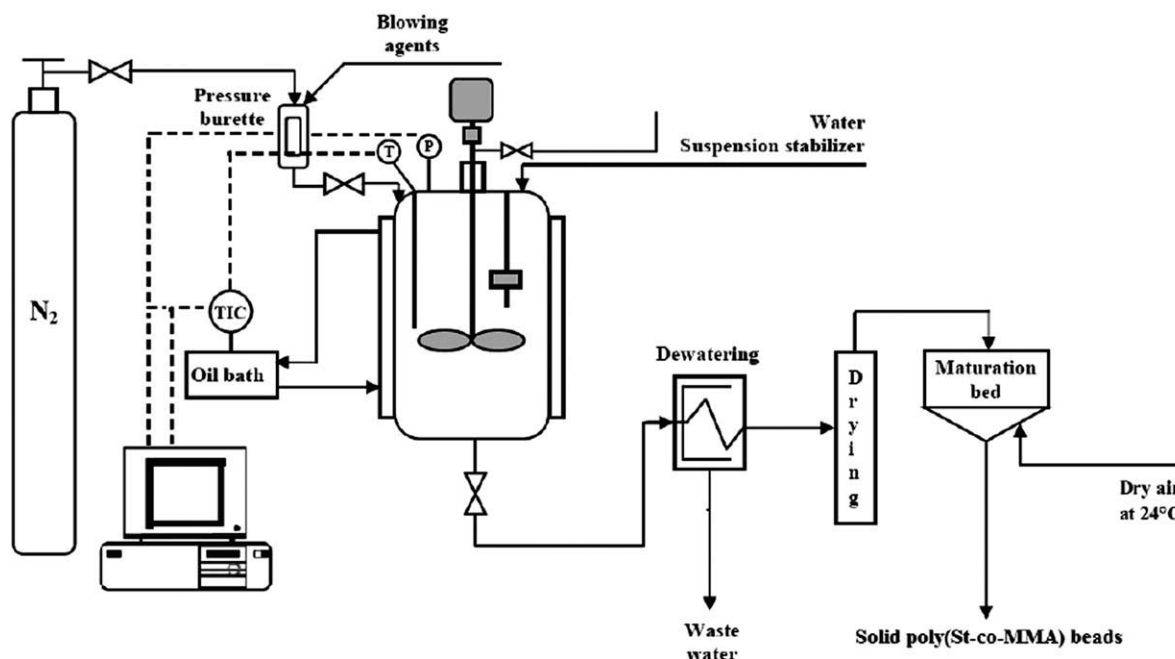


Figure 2 Batch suspension polymerization set-up.

copolymer was acidified to a pH of 1.6–2.0 and after 15 min holds time, the residue was washed with water and dewatered, dried at a temperature of less than 40°C to obtain foamable resin pellets. The mean particle size (MPS) and particle size distribution of resulting beads were determined by sieving the beads through an adequate set of different mesh sizes. The overall production set-up consisted of a 1-L high temperature-high pressure suspension polymerization reactor (Fig. 2).

### Ampoule polymerization

The time-conversion data were obtained from ampoule experiments. All isothermal bulk copolymerizations of St-MMA with and without mixed pentanes isomers were carried out in 5-mm outer diameter (O.D.) glass ampoules and conducted at constant scaled up temperature, 80°C. The ampoule contents were degassed through the standard freeze-thaw cycles and sealed under a maximum pressure of  $10^{-4}$  Torr. For the experiments with mixed pentanes isomers, the blowing agent was added to the ampoule mix through a microsyringe at the beginning of the reaction. After addition, the reaction mixture was homogenized through agitation, to avoid possible phase separation. In such an experiment,<sup>42–45</sup> ampoules containing monomer, initiator, and mixed pentanes were placed into a constant temperature medium and sampling interval of once every 30 min for low conversions and 5 min during gel effect was utilized. The ampoules were removed from the bath at the required times and immediately quenched in liquid nitrogen. These samples were collected in presteri-

lized 20-mL glass scintillation vials. The polymerization reactions in the withdrawn samples were quenched by adding 0.1 mL of a 2% hydroquinone solution in methanol and shaking it manually. The samples were then immersed in an ice-water mixture for ~ 30 min and stored in a refrigerator at a temperature below 10°C prior to analysis.

### Characterization

After drying the final product, the size distribution of the synthesized beads was determined by sieving and recording the MPS. The MPS was calculated using the following equation:<sup>46</sup>

$$D_m = \frac{\sum(P_i D_i)}{100}, \quad (1)$$

where  $P_i$  is the residual weight percent on each sieve and  $D_i$  is the MPS for each sieve. The MPS,  $D_i$ , is given by:

$$D_i = (d_i + d_{i+1})/2, \quad (2)$$

where  $d_i$  is the nominal diameter of  $i$ th sieve.

The particles compositions were determined by  $^1\text{H}$ -nuclear magnetic resonance spectroscopy ( $^1\text{H}$ -NMR); the particles were dissolved in deuterated chloroform,  $\text{CDCl}_3$ ; the spectra of the samples were obtained with a Brüker (Advance DPX) NMR spectrometer working at 500 MHz. The molar percentage of monomer incorporated to the particles was determined using the peak of  $\text{OCH}_3$  group (at 3.6 ppm), and the peaks correlated to the aromatic

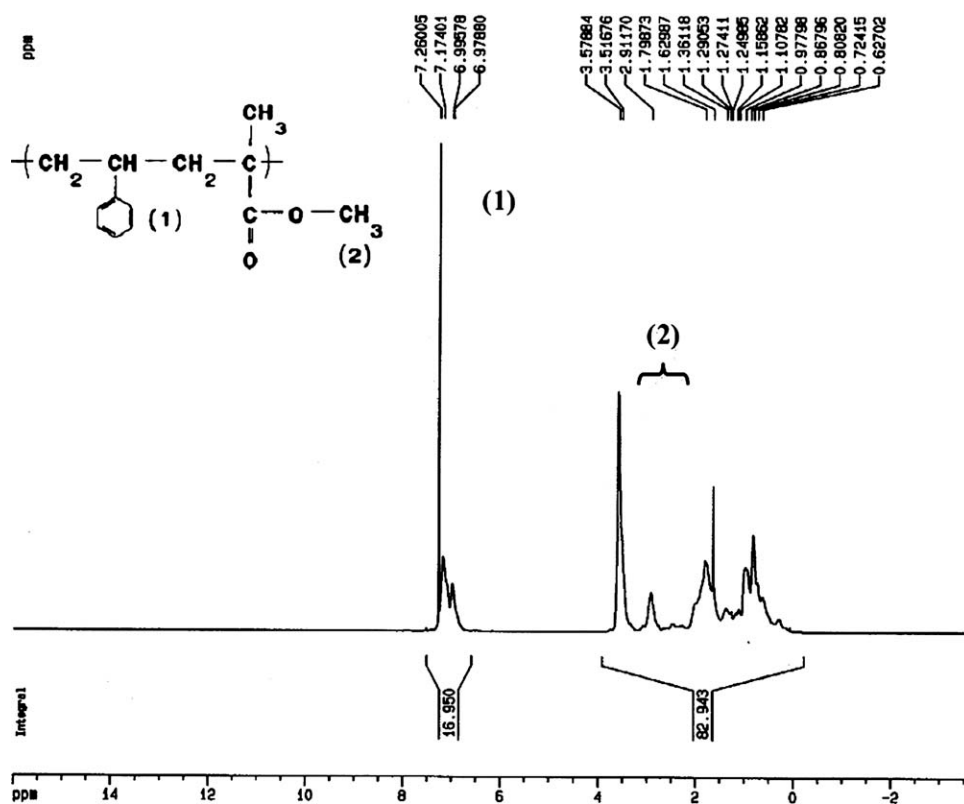


Figure 3  $^1\text{H-NMR}$  spectrum of synthesized poly(St-co-MMA) obtained from run 3.

ring (between 7.5 and 6.5 ppm). The peaks correlated to the  $\text{CH}_2$  and  $\text{CH}$  groups were used to verify the integration error. The copolymer composition from the  $^1\text{H-NMR}$  spectrum was evaluated using the following equation:<sup>47</sup>

$$\frac{m_1}{m_2} = \frac{A_1 \times 1/5}{(A_2 - A_1 \times 8/5) \div 8}, \quad (3)$$

where  $m_1$  and  $m_2$  are the mole fractions of St and MMA in copolymer, respectively, and  $A_1$  is the integrated area of the phenyl protons of St unit at 6.5–7.5 ppm and  $A_2$  is the integrated area of the all protons of the copolymer.

In order to obtain quantitative information about the total release of gaseous products, thermogravimetric measurements were used. The weight loss of a sieve fraction of 150–500  $\mu\text{m}$  lost foam beads was monitored using Perkin Elmer Pyris Diamond TG/differential thermal analysis (DTA) under a nitrogen flow of 50 mL/min. The temperature program started at 30°C at a heating rate of 20°C/min to 600°C.

In order to identify the nature of volatiles measured by TG/DTA analysis and precise calculation of pentane content and residual monomer, VOCs were measured by GC with MS detection using a TraceGC 2000 (Thermo Finnigan, Milano, Italy) gas chromatograph coupled to a Trace Plus (Thermo Finnigan,

Austin TX, US) single quadrupole mass spectrometric detector. Data acquisition, processing, and evaluation were carried out using Xcalibur Data System Version 1.3 (Thermo Finnigan, Austin TX). The analytes were separated on a Restek Stabilwax fused-silica capillary column (60 m  $\times$  0.32 mm ID, 0.5- $\mu\text{m}$  film thickness, Restek, Bellefonte PA). The temperature program used for separation of the target compounds was as follows: 1 min at 40°C, 7°C/min to 130°C, 7°C/min to 180°C, and holding at 180°C for 8 min. The GC was equipped with a programmable temperature vaporizer BEST PTV (Thermo Quest, Austin TX, US) that was used in the splitless mode at an injection port base temperature of 200°C and a splitless time of 1.5 min. A 2-mm inner diameter (I.D.) deactivated silcosteel linear (BGB, Anwil, Switzerland) was used, and the transfer time was adjusted to 20 s. Carrier gas was Helium 5.0 with a constant flow rate of 1.5 mL/min. Dissolution-precipitation extraction was carried out with chloroform/methanol (1 : 3). Samples (1.5 g) were placed in a sealed glass container and 10 mL of chloroform were added for dissolving the polymer. The solution was slightly shaken to achieve complete dissolution. At this stage, it is necessary to wait until sample is totally dissolved. Finally, 30 mL of methanol were added, and the solution was vigorously shaken for a few seconds in order to reprecipitate copolymer. The solution was let to rest until two clear phases were

TABLE II  
The Compositions of the Selected Synthesized  
Copolymer Beads

Run	$A_1$	$A_2$	Copolymer composition	
			MMA	St
1	1	0.257	0.6837	0.3163
2	0.956	0.345	0.6882	0.3118
3	0.856	0.398	0.6864	0.3136

observed: one precipitate and one clear liquid. After separation of two phases (1–2 h), an aliquot of the solution was transferred to the GC-MS for analysis of St, MMA, *n*-pentane, and *i*-pentane.

## RESULTS AND DISCUSSION

### Copolymer composition

Figure 3 shows a typical  $^1\text{H-NMR}$  spectrum of the St-MMA copolymer obtained from run 3. The peaks at 7.1 and 3.6 ppm, corresponding to  $\text{C}_6\text{H}_5$  and  $\text{OCH}_3$ , can be observed. The peak at 2.8 ppm, absent in the  $^1\text{H-NMR}$  spectra of both relevant homopolymers,<sup>48,49</sup> can be observed in the copolymer spectrum. This has been assigned to the  $\text{OCH}_3$  group of polymethyl metacrylate (PMMA) bonded to the PS segment.<sup>50</sup> Opresnik and Sebenik<sup>51</sup> also showed that this peak could be much more clearly seen in the  $^1\text{H-NMR}$  spectra of a St-MMA random copolymer rather than of a St-MMA block copolymer.

Compositions of the copolymers were evaluated, and the results of  $^1\text{H-NMR}$  spectroscopy for selected runs are summarized in Table II. The calculated copolymer compositions were found to be fairly close to the monomer feed ratios. This suggests that both monomers undergo propagation at similar rates.

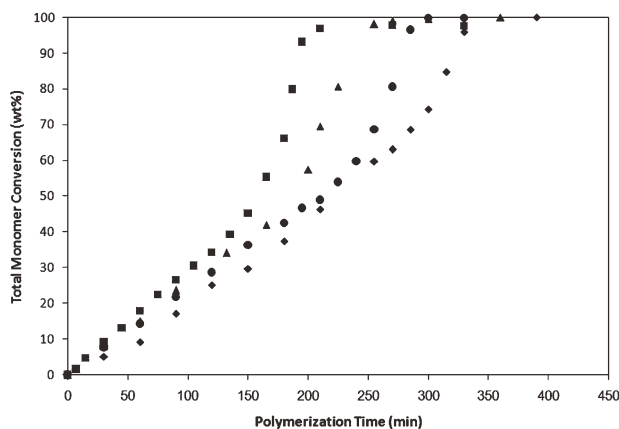


Figure 4 Effect of pentane concentration added from the beginning of the polymerization on copolymerization rate of St/MMA. Experimental monomer conversion are presented for 0 (■), 5 (▲), 10 (●), and 15 (◆) wt% pentane.

### Ampoule polymerization

Residual monomer conversion was measured from kinetic behavior investigation through ampoule polymerization technique. At very high conversions and below the glass transition temperature  $T_g$ , when, due to the growing amount of polymer chains, the solution enters the so-called glassy state, also the monomer diffusion becomes limited. Consequently, the rate of polymerization diminishes until the reaction freezes. This phenomenon is called glass effect and causes a significant conversion limitation for below- $T_g$  polymerizations. So, it is known that the free radical polymerization reactions rarely proceed to completion, leading to the presence of unreacted residual monomer in the polymeric material.<sup>52</sup> Monomer conversion rate is one of the parameters used for evaluating the free radical suspension polymerization process and can be obtained by a gravimetric analysis. In this work, an ampoule polymerization technique was used for the determination of conversion history and residual monomer level in the final copolymer product. The fractional conversion was determined by flash evaporation under reduced pressure and rigorous vibration, drying, and weighing the resultant polymer.

Figure 4 shows a complete set of time-conversion data for the four copolymerizations obtained from ampoule polymerization with and without presence of pentane isomers. Because of the small difference

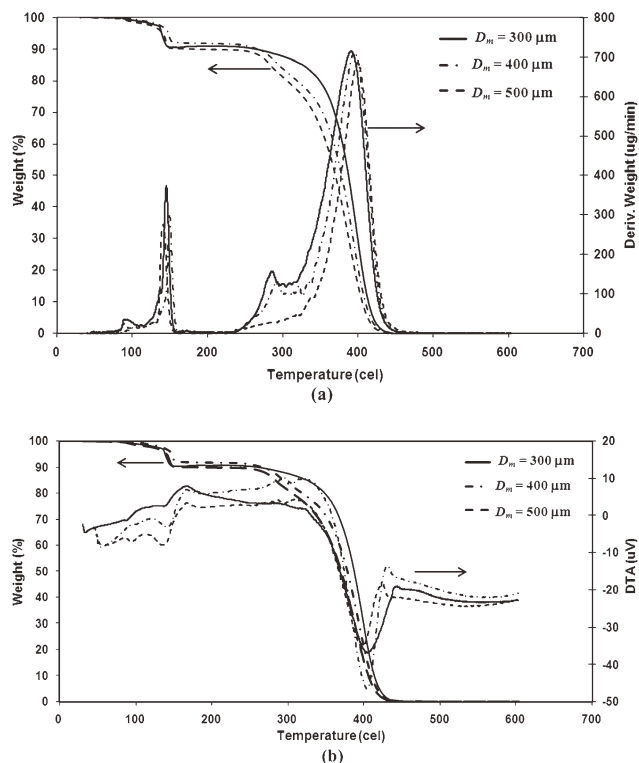


Figure 5 Thermogravimetry analysis of synthesized lost foam beads. (a) TG-DTG curves and (b) TG-DTA curves.

**TABLE III**  
**TG Results for Lost Foam Beads in Nonisothermal Process at N<sub>2</sub> Atmosphere (50 mL/min)<sup>a</sup>**

Beads	First event $T_{\text{ons}} - T_f$ (°C)	Second event $T_{\text{ons}} - T_f$ (°C)	Third event $T_{\text{ons}} - T_f$ (°C)	$\Delta m$ (%)		
				First step	Second step	Third step
300 $\mu\text{m}$	48–120	120–165	240–450	2.31	7.65	90
400 $\mu\text{m}$	30–120	120–170	240–450	1.41	8.26	90.3
500 $\mu\text{m}$	25–135	135–163	240–450	3.64	5.83	90.75

<sup>a</sup>  $T_{\text{ons}}$ , temperature onset of weight loss;  $T_f$ , temperature final of event;  $\Delta m$ , mass loss.

in molar mass between St and MMA, this conversion will be treated as a mole fraction of monomer converted, irrespective of composition.

On addition of pentane isomers, the free volume of the system increases<sup>53</sup> and so does the molecular mobility of the polymer chains. Because the small molecules of pentane diffuse across the polymer coils, the plasticizing effect thus induced facilitates the translational diffusion of the growing radicals necessary to approach each other and terminate. As a result, the onset of the translational diffusion controlled termination reactions is delayed and a decrease in the polymerization rate must be expected according to the decrease of both monomer concentration and initiation reaction rate. The decrease in the polymerization rate will proceed up to the conversion at which the free volume of the system is such that the termination reactions become translational diffusion controlled despite the plasticizing effect of pentane isomers. However, if the concentration of pentane isomers is high enough, this point may never be reached, in which case a progressive decay of the polymerization rate must be observed.

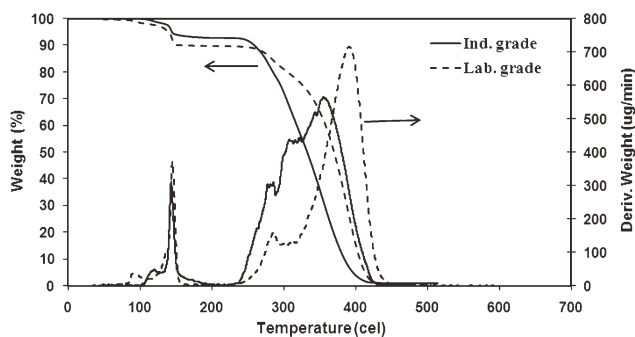
Figure 4 also shows the effect of the concentration of pentane, added from the beginning of the polymerization, on the conversion history of the bulk St/MMA initiated with BPO at 80°C. In the absence of pentane isomers, the curve shows the onset of the gel effect at about 50% conversion and the terminal conversion does not lead to completion (100%). When 5 wt % pentane isomers are present, two main differences in the conversion history are observed: first an initial slight decrease in the polymerization rate and second decrease of severity occurrence of gel effect. However, in the presence of 5 wt % pentane, terminal conversions close to 100% were obtained despite the decrease in reaction rate. The initial decrease in polymerization rate, in addition to lower monomer and initiator concentrations due to the presence of pentane in the system, is due to an increase in the segmental diffusion controlled termination rate, caused by the decrease in growing polymer coil sizes in the pentane plasticized system. This decrease in coil sizes is brought about by the fact that monomer/pentane mix is a poorer solvent

for St/MMA copolymer than the pure monomer.<sup>17,18</sup> In a poorer solvent, the coil sizes decrease and the segmental diffusion increases.

The curve for 10 wt % pentane in the initial polymerization mix shows the similar initial decrease in polymerization rate and decrease of gel effect, with terminal conversion approaching to 100 wt %. It was expected that further increases of pentane isomers lead to further alleviation of gel effect due to higher plasticizing effect of pentane equivalent to what it is observed in Figure 4 for 15 wt % presence of pentane. Nonetheless, terminal conversions close to 100% were obtained notwithstanding the further decrease in reaction rate. Contrary to what was expected, in the all cases of our polymerization recipes with presence of blowing agent, the radical polymerization reaction proceeds to completion without any significant of residual monomer traces in the final copolymer product.

### Thermogravimetry

TGA curves (TG and DTG) are depicted together with DTA signals in Figure 5(a,b). The DTA signal indicates whether a weight loss measured by the thermobalance is an exothermic or endothermic process. Figure 5(a), the weight loss curve with increasing temperature under nitrogen atmosphere, shows that the lost foam precursor decomposed in three separate stages initiating at different temperatures for 300-, 400-, and 500- $\mu\text{m}$  bead sizes. The two first weight losses are presumably due to exhaustion of



**Figure 6** Comparison of the thermal behavior of a commercial grade lost foam with the synthesized beads.

**TABLE IV**  
**Results for the Thermal Stability of Industrial and Laboratory Grade Lost Foam Beads**

Sample	First and second steps			Third step			$T_{\max}$ (°C)
	$T_{v0.5}$ (°C)	$T_{v1.0}$ (°C)	$T_{v2.0}$ (°C)	$T_{v0.5}$ (°C)	$T_{v1.0}$ (°C)	$T_{v2.0}$ (°C)	
Laboratory	129	135	141	264	274	332	394
Industrial	135	139	141	246	253	268	359

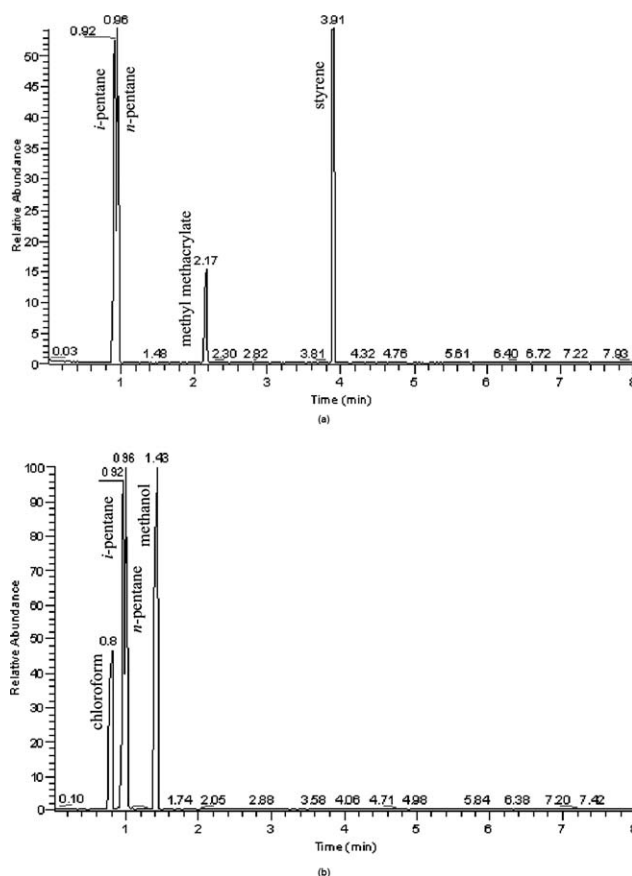
the low boiling point species that involve a mixture of *n*- and *i*-pentane (in the certainly absence of residual monomer with respect to ampoule polymerization results). First, it starts at  $\sim 91^\circ\text{C}$  and has its maximum rate between  $140\text{--}180^\circ\text{C}$ , which is in agreement with exhaustion of *i*-pentane (b.p.:  $28^\circ\text{C}$ ) and *n*-pentane (b.p.:  $36.1^\circ\text{C}$ ), respectively. Second, those are an endothermic weight losses, as can be seen from the DTA curve [Fig. 5(b)], a fact, which underlines that this weight loss due to the volatile release. The second weight loss on the other hand, is exothermic. The exothermic peak appearing at the temperature range between  $250$  and  $500^\circ\text{C}$  could be attributed to a scission mechanism of a polymeric chain like poly(St-*co*-MMA) copolymer.<sup>17,18</sup> The losses of masses at different stages as shown by the TG/DTA curve of untreated lost foam beads of different size are shown in Table III.

The polymer samples coming from the laboratory scale reactor were analyzed in the analytical facilities of the industrial partner according to a method validate for commercial polymers. This allowed the direct comparison between the products from the laboratory scale reactor to industrial scale produced lost foam. The specifications concerning the thermal stability of a product are given by characteristic value, which quantify the weight loss at certain criteria and can be easily compared for different samples. These criteria are  $T_{v0.5}$ ,  $T_{v1.0}$ , and  $T_{v2.0}$ : the temperature where the rate of weight loss is of  $50\ \mu\text{g}/\text{min}$ ,  $100\ \mu\text{g}/\text{min}$ , and  $200\ \mu\text{g}/\text{min}$ , respectively, and  $T_{\max}$ : the temperature of maximum rate of weight loss.

Apart from the relative weight loss suffered at a given temperature, the rate of weight loss is also important, because the exposure of the polymer to elevated temperatures is usually kept rather short in molding process. Figure 6 shows the typical result from a thermogravimetric analysis of an industrial grade lost foam with an average particle size of  $300\ \mu\text{m}$  that coming from a  $250\text{-L}$  pilot scale reactor and synthesized sample in laboratory scale reactor (Fig. 2) with high purity laboratory grade raw materials and a same average bead size. As can be seen from DTG curve, below  $250^\circ\text{C}$  in the first two stages of decomposition, the industrial sample lose less than  $300\ \mu\text{g}$  of its weight per minute. These values were not precisely match with the polymer produced in this research. Especially, the weight loss rates  $T_{v0.5}$ ,

$T_{v1.0}$ , and  $T_{v2.0}$  were reached at lower temperatures (compare Table IV), which might be due to the fact that the laboratory grade lost foam polymer contains rather large amounts of blowing agent contents, at least in comparison to industrial polymer, which has to be reached to lower densities at the end of pre-expansion process and final casting pattern.

In contrast to initially two stages, the values  $T_{v0.5}$ ,  $T_{v1.0}$ , and  $T_{v2.0}$  in the third stage of decomposition, that is, the thermal lability between  $250$  and  $450^\circ\text{C}$ , were reached at considerably higher temperatures (Table IV). It is evident that, for synthesized copolymer, the thermal stability is considerably improved in the interim of higher blowing agent content.



**Figure 7** GC-MS total ion chromatogram (TIC) of the synthesized lost foam beads. (a) Chromatogram of standard solutions and (b) chromatogram of target compound.



TABLE V  
Volatile Organic Compounds Released from Expandable Poly(St-co-MMA)

Retention time (min)	Boiling point (°C)	Molecular weight (g/mol)	Identification	
			Common name	IUPAC name
0.8	61.2	119.38	Chloroform	Trichloromethane
0.92	28.0	72.15	<i>i</i> -Pentane	2-Methylbutane
0.96	36.1	72.15	<i>n</i> -Pentane	Pentane
1.43	64.7	32.05	Methanol	Methanol

### Chromatography analysis

Analyses of extracts were performed by GC-MS total ion chromatograms (TICs). Calibration curve for St, MMA, *n*-pentane, and *i*-pentane was run at five concentration levels using appropriately diluted standards. For dissolution-precipitation extraction, calibration standards of volatiles were prepared in chloroform/methanol (1 : 3). Each concentration level was injected in triplicate, and chromatographic peak areas were fitted by linear regression. The linearity range was 0.4–20 µg/g with correlation coefficients higher than 0.999. No sample clean-up was done on the extracts prior to analysis. VOC detection of a 300-µm bead size sample was carried out, and obtained chromatogram under optimized conditions is illustrated in Figure 7.

Identification of compounds was carried out by comparison of retention times and mass spectra of standards, study of the mass spectra, and comparison with data in the Xcalibur spectra library. The retention data, the boiling points, the molecular weights of compounds, and summarizing of identification results are given in Table V. As can be seen from Table V, the major VOCs found in Figure 7 were *n*-pentane and *i*-pentane without any traces of residual St and MMA monomers.

Combination of TG/DTA data with the information obtained from GC-MS TICs allows the precise identification of gaseous products and their assignment to thermogravimetrically detected decomposition steps. The TG curve shows three significant steps of mass loss during the thermal decomposition of lost foam bead in the temperature range up to 500°C performed at heating rate 20°C/min (Figs. 5 and 6). The release of only pentane isomers as gaseous products (comply with the known mass spectrum<sup>54</sup>) during the thermal decomposition in the two first stages was also established by obtained peaks at *m*72-*m*75. The absence of detectable signals at *m*100 and *m*104 indicates a negligible concentration of MMA and St traces, respectively, in the final lost foam beads that it can be referred as best candidate in order to meet environmental and toxicological requirements for consumer products.

### CONCLUSIONS

An analytical method for the determination of blowing agents content and monomer residual in synthesized lost foam beads has been developed using TG analysis (TGA) and dissolution-precipitation extraction followed by GC-MS technique. TG also showed that the lost foam beads thermally decompose in three steps, which are due to the release of *i*-pentane, *n*-pentane, and scission of the polymer chains. The TG/DTA data clearly illustrated the improved thermal stability of the synthesized beads in the side of lower density of molding pattern in respect to industrial grade of lost foam copolymer. Calibration curve was run at five concentration levels using appropriately diluted standards. The chromatographic peak areas were fitted by linear regression with a higher linear regression coefficient ( $R^2 > 0.999$ ). The separation and identification analysis developed by the TG/DTA-GC/MS combined method had identified any traces of residual monomers and toxic products evolved in the decomposition of the synthesized lost foam copolymer. The total volatile content (VOC) present in the beads pertains to two types blowing agents used in the polymerization course was quantified accurately. The rapid, simple, and cost-effective method with good repeatability can be applied to the process control of industrial expandable poly(St-co-MMA) production and to measure and screen residual monomers and VOCs in the environment.

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