

# On-Line Conversion Monitoring Through Ultrasound Propagation Velocity Measurements in Emulsion Polymerization

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## SYNOPSIS

An on-line sensor for estimating conversion from measurements of ultrasound propagation velocity in emulsion polymerizations has been developed. The sensor does not require a sampling circuit, because it can be directly plugged in the reacting mixture. The performance of the sensor has been tested by comparison with off-line gravimetric measurements of conversion under various operating conditions. These include the homopolymerization of methyl methacrylate and vinyl acetate, with different values of the monomer to water ratio and the initial concentrations of emulsifier and initiator. The results obtained using either an empirical calibration curve or a suitable *a priori* model indicate excellent reliability of the sensor with somewhat lower accuracy at low conversion values, i.e., when monomer droplets are present. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In order to improve polymer quality, accurate control techniques<sup>1,2</sup> and sensors, able to monitor on-line the quality of the polymer being produced in the reactor,<sup>3</sup> are needed. In this context, conversion, defined in a batch system as the weight of polymer produced with respect to the total weight of monomer initially fed to the reactor, is a key variable to follow the evolution of the reacting process. Its monitoring allows one to overcome the irreproducibilities typical of these reacting systems, for example, differences in the initial induction time. Moreover, the knowledge of the conversion value on-line considerably simplifies the control of semibatch polymerization reactors. Examples include the implementation of monomer addition policies to produce polymers with constant instantaneous composition<sup>4</sup> or of chain transfer agent to control the molecular weight distribution.<sup>5</sup>

The most common technique for measuring conversion off-line is gravimetry. Various techniques have been developed for measuring on-line conversion in emulsion polymerization reactors. Gas chromatography provides conversion together with overall monomer composition when quantitative sampling is performed. The development of an automatic sampler and of the corresponding sampling circuit<sup>6,7</sup> is required, and the measured values become available with a delay that may be significant, particularly in semibatch reactions. Calorimetry is probably the simplest on-line technique for measuring conversion.<sup>8</sup> However, its application requires treating the polymerization reactor as a calorimeter, which is often not feasible, particularly in industrial applications. Densimetry, originally developed for homopolymers<sup>9</sup> and subsequently extended to copolymers,<sup>10</sup> is also an attractive on-line technique. It provides fast responses with about one measurement per second, thus resulting in a practically continuous monitoring of the conversion evolution. However, this technique also needs the development of a specific sampling circuit, requiring periodic assistance for preventing fouling, which may be rather onerous, particularly in industrial environments.

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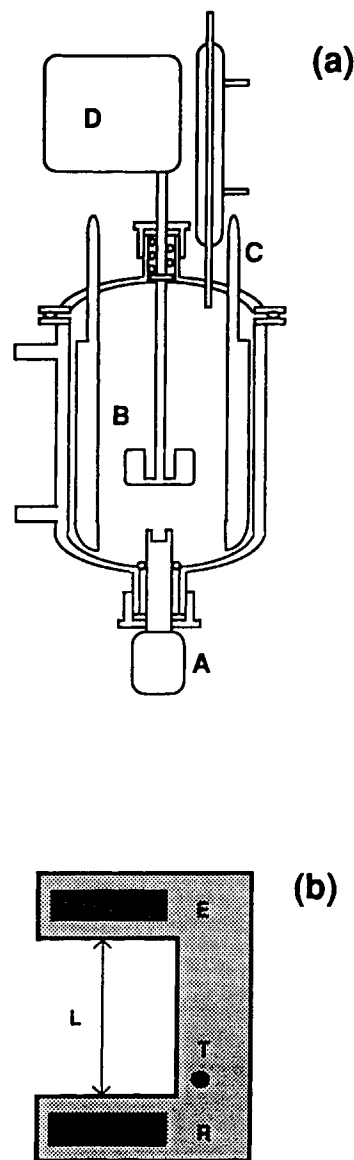
A potential alternative to previous techniques is to estimate monomer conversion through measurements of ultrasound propagation velocity in the emulsion. In a homogeneous system, this velocity depends upon the inverse of the square root of the product between density and compressibility, which both change as monomer is transformed into polymer, thus providing a relation between sound propagation velocity and monomer conversion. Applications of this principle have been reported earlier in the literature.<sup>11-15</sup> In the last work by Hauptmann et al.,<sup>14</sup> both sound velocity and attenuation are measured in the case of vinylacetate polymerization using a sensor based on the pulse traveling technique. The reported data refer to both low and high conversion values. In the first case, qualitative informations about the nucleation process are obtained through the attenuation measurements. In the second case, where significant difficulties in measuring attenuation values are reported, conversion is estimated by combining the sound velocity data with an empirical model.

In this work, applications to methyl methacrylate (MMA) and vinylacetate (VAC) homopolymerizations are discussed. The adopted sensor is a prototype manufactured by Labor für Messtechnik of Graz (Austria). It operates at 3 MHz pulse frequency, with a sound path length less than 1 cm and provides about five measurements per minute. The measuring probe can be directly plugged in the reacting mixture, without requiring a sampling device, thus making its use particularly simple and suitable for industrial applications. A model is developed to correlate velocity of ultrasound propagation to conversion in emulsion polymerization systems. The model accounts for the dispersed nature of the system as well as for the significant variation of the polymer compressibility during the reaction. Finally, the capabilities of the proposed sensor to monitor conversion are tested using either an empirical or a model based calibration procedure.

## EXPERIMENTAL APPARATUS

### Reacting System

The adopted experimental apparatus is shown in Figure 1(a). The probe of the instrument (A) is located at the bottom of a 2 L glass jacketed reactor (B) where, due to the locally high mixing, the presence of gas bubbles on the piezoelectric crystals of the measuring cell is minimized. Gas bubbles between the transducers produce disturbances in the



**Figure 1** (a) Experimental apparatus. A: sound speed sensor; B: reactor; C: baffles; D: stirrer. (b) Sketch of the probe. E: emitter; R: receiver; L: distance between transducers; T: thermocouple.

measured values of ultrasound propagation velocity. The temperature in the reactor is controlled by a thermostatic bath operating on the water stream circulating in the reactor jacket. The reactor is equipped with four glass baffles (C) and the stirrer (D) is a radial glass blade. A stirring speed of 300 rpm has been adopted in all the reported experimental runs. Commercial MMA and VAC (both RPE grade) have been used as received, without removing the inhibitor. Water has been deionized and distilled while emulsifier (Sodium Lauryl Sulphate—SLS) and initiator (Potassium Persul-

**Table I Characteristics of the Sensor of Sound Propagation Velocity**

Single pulse frequency	3 MHz
Pulsing frequency	300 Hz
Sampling rate	5.7 data/min
Operating temperature range	0 ÷ 110°C
Probe material	Astelloy C
Distance between transducers	0.8 cm

phate—KPS) have been used without further purification.

### Sensor for Measuring the Ultrasound Propagation Velocity

The resolution of the instrument used to measure the sound propagation velocity is  $\pm 0.01$  m/s, while the reproducibility has been estimated as  $\pm 1$  m/s. A sketch of the measuring probe is shown in Figure 1 (b), while the main instrument characteristics are summarized in Table I. The probe is equipped with a thermocouple to measure the temperature nearby the receiving crystals, with resolution  $\pm 0.1^\circ\text{C}$ . Ultrasound velocity is measured through a modified version of the pulse traveling technique, where the time needed by an ultrasonic pulse to travel between two piezoelectric transducers at fixed distance,  $L$  is measured. In this apparatus,  $L$  is equal to 8 mm, and the traveling time of the sound wave is measured using a specific technique based on a train of single pulses.<sup>16</sup> The triggering is done approximately 300 times per second. The probe is connected with an electronic device that estimates the velocity value and sends it, together with the temperature value, to a personal computer 5.7 times per minute through a standard RS232C communication port.

## EXPERIMENTAL RESULTS

In order to explore the capabilities of this sensor with respect to conversion monitoring, seven hom-

opolymerization reactions have been performed, using either MMA or VAC, according to the recipes summarized in Table II. During each experimental run, off-line gravimetric analyses have been performed so as to provide an independent evaluation of conversion.

In order to have a reliable sensor, it is necessary to correct the measured values of sound propagation velocity for the temperature changes, which may be significant, particularly in industrial units. Thermal variations affect both the sensor characteristics (i.e., the distance  $L$  between the transducers) as well as the parameters of the equations relating sound speed to conversion, i.e., mainly density and compressibility. The first aspect is accounted for directly by the software supervising the measuring apparatus. About the second one, an empirical correction based on the difference between the reference (i.e., the reaction or set-point temperature) and the actual temperature value has been developed. In particular, the ultrasound propagation velocity in the emulsion,  $v_E$ , is estimated by the following linear equation:

$$v_E = \hat{v}_E - \alpha(T - T_R) \quad (1)$$

where  $\hat{v}_E$  indicates the measured velocity value,  $T_R$  the reference temperature,  $T$  the actual temperature in the reactor, and  $\alpha$  a constant factor. This has been estimated experimentally by measuring the variation of the ultrasound velocity in a model system (typically, a spent latex of the same homopolymer with the same polymer to water ratio) with the temperature, in a reasonable range around the reference value ( $40 \div 60^\circ\text{C}$ ). The following  $\alpha$  values have been estimated: 3 m/sC for MMA and 5 m/sC for VAC.

In the following subsections, the reproducibility of the experiments is first discussed and then the effect of various variables, which are typically involved in determining the recipe of an emulsion polymerization reaction, is examined.

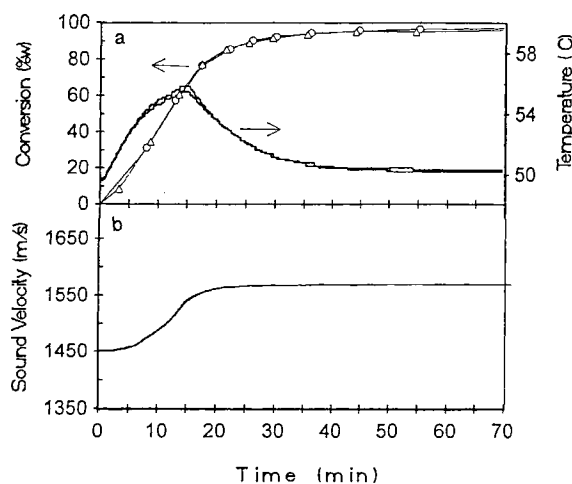
**Table II Recipes of the Experimental Polymerization Runs**

Run	Monomer	$M^0$ [g]	$M^0/W^0$	SLS [g]	KPS [g]
92	MMA	106	0.144	4.5	1.1
94	MMA	106	0.144	4.5	1.1
95	MMA	53	0.072	4.5	1.1
96	MMA	212	0.288	4.5	1.1
97	VAC	105	0.144	4.5	1.1
98	VAC	105	0.144	9.0	1.1
99	VAC	105	0.144	4.5	1.9

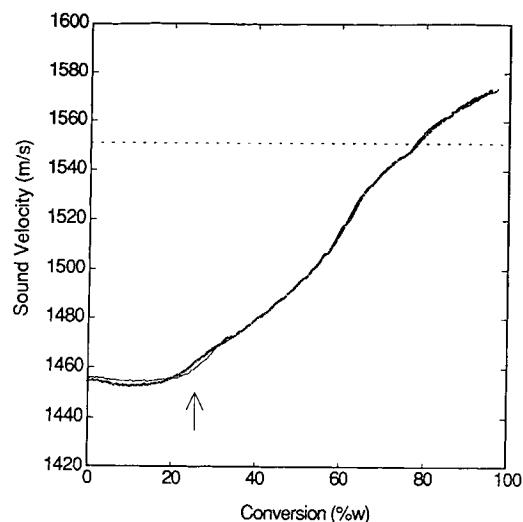
## Reproducibility

Data of conversion (by gravimetry), temperature, and ultrasound propagation velocity are shown as a function of time in Figure 2 for two identical MMA polymerizations (runs 92 and 94 in Table II). The continuous curves for temperature and sound velocity represent on-line measurements. It can be seen that, for the polymerization runs at hand, the overall change of sound velocity during the entire polymerization reaction is about 100 m/s. The temperature in the reacting medium increases in the first 15 min because of the heat produced by the reaction and the limited heat removal capacity of the thermostating circuit. The continuous curves of conversion as a function of time have been obtained by discrete linear interpolation of the values measured off-line through gravimetry. It can be seen that the sound propagation velocity–time curve is somehow similar to the conversion–time curve.

The same data are reported in terms of velocity of sound propagation as a function of conversion in Figure 3, where a nonlinear behavior is evidenced. The dotted straight line in the same figure indicates the value of the sound velocity in the initial solution, containing SLS and KPS alone, while the arrow indicates the conversion value where oil droplets disappear, estimated through the model discussed in the next section. It can be noted that, before the oil droplets disappearance, the sensitivity of the instrument is rather low, i.e., large variations of conversion correspond to small changes of sound velocity. On the other hand, the ultrasound propaga-



**Figure 2** Comparison between runs 92 and 94. (a) Conversion from gravimetry ( $\circ$  = run 92;  $\triangle$  = run 94) and temperature and (b) sound propagation velocity vs. reaction time.



**Figure 3** Sound velocity vs. conversion for runs 92 and 94. ( $\cdot\cdot\cdot$ ) = sound velocity value in the aqueous solution of SLS and KPS. The arrow indicates the disappearance of oil droplets.

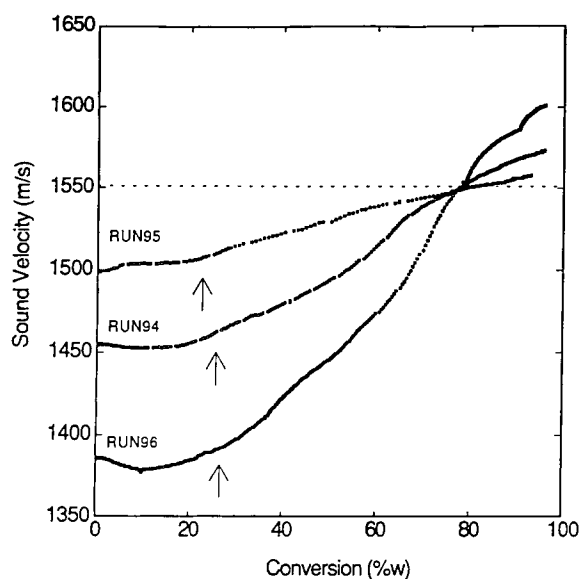
tion velocity vs. conversion curve is well reproduced for identical recipes: the obtained differences are, in fact, in the range of the experimental error characteristic of both the gravimetric technique and the measuring device adopted.

## Influence of Monomer to Water Ratio

Let us first analyze the effect of the overall amount of monomer in the reactor on the ultrasound propagation velocity. Three polymerization reactions of MMA with different monomer to water ratio have been performed. These correspond to runs 94, 95, and 96 in Table II, where the monomer to water ratio is equal to 0.144, 0.078, and 0.288, respectively.

The experimental findings are summarized in Figure 4 in terms of sound velocity as a function of conversion, where we iterate that the conversion values have been obtained by discrete linear interpolation of the gravimetric measurements. In the same figure, the dotted straight line represents the measured sound velocity in the aqueous solution containing SLS and KPS alone, while the arrows indicate the estimated conversion values where oil droplets disappear.

From the data shown in Figure 4, it appears that, as the monomer to water ratio increases, the overall change of the sound propagation velocity and the slope of the curve representing sound velocity as a function of conversion increases, thus indicating a larger sensitivity of the sensor under examination to conversion changes. This feature is particularly

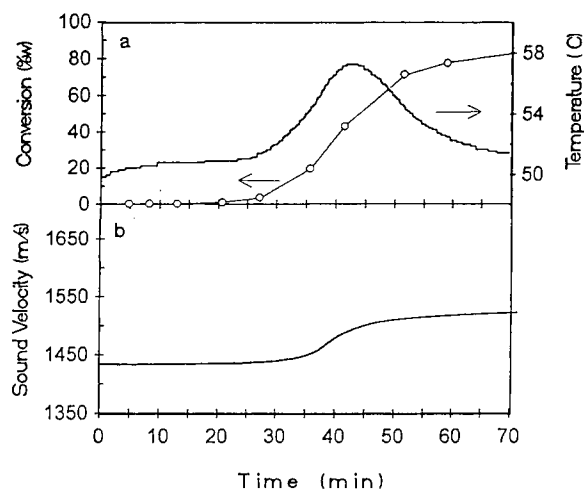


**Figure 4** Effect of monomer to water ratio: runs 94, 95 and 96. (· · ·) = sound velocity in the aqueous solution of SLS and KPS. The arrows indicate the disappearance of oil droplets.

attractive with respect to industrial applications, where the monomer to water ratio is usually even larger than the maximum value considered in this figure. Moreover, we may note that the three curves in Figure 4 cross each other at the same conversion value where the corresponding sound propagation velocity becomes equal to that in the aqueous solution of emulsifier and initiator alone. This can be explained by considering that the velocity of sound propagation in the polymer particles changes as the monomer to polymer ratio decreases, i.e., as conversion increases. Since, in this case, the sound velocity value in water lies between those in monomer and polymer, there exists a particular conversion value where the sound propagation velocity in the polymer particles becomes equal to that in the aqueous solution. For the system under examination, such a conversion value is equal to about 75%, which, as shown in Figure 4, is independent of the value of the monomer to water ratio.

### Influence of Emulsifier and Initiator

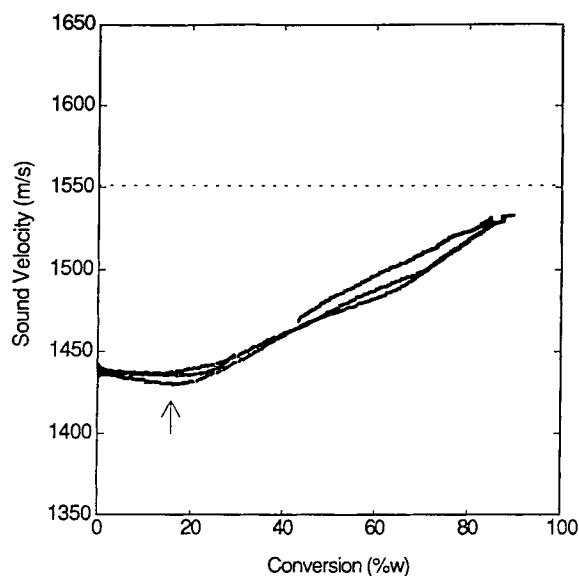
In order to investigate the effect of emulsifier and initiator, in the amounts that are typically used in emulsion polymerization processes, three polymerization reactions of VAC have been performed. By taking run 97 as the base case, the initial amount of SLS has been doubled in run 98, while that of KPS has been doubled in run 99, as reported in Ta-



**Figure 5** Polymerization run 97. (a) Conversion from gravimetry (O) and temperature and (b) sound propagation velocity vs. reaction time.

ble II. The above polymerization reactions have largely different conversion (by gravimetry) vs. time curves. In particular, run 97, shown in Figure 5, exhibits the largest induction time (about 25 min), probably due to the low initiator concentration in combination with the presence of impurities such as residual monomer inhibitor or oxygen.

The obtained results are summarized in Figure 6 in terms of sound propagation velocity as a function of conversion. It is apparent that, despite the largely



**Figure 6** Effect of emulsifier and initiator: runs 97, 98 and 99. (· · ·) = sound propagation velocity in the aqueous solution of SLS and KPS. The arrow indicates the disappearance of oil droplets.

different kinetic behaviors, the three polymerizations lead to almost identical sound velocity vs. conversion curves. This is, indeed, a rather convenient feature for developing a sensor that estimates conversion from sound velocity data. Note in passing that, in contrast with the case of MMA, when using VAC, the velocity of sound propagation in the emulsion remains always lower than the corresponding value in the aqueous solution of emulsifier and initiator alone (dotted straight line).

### Influence of Monomer Type

By comparing the results obtained in two runs with equal recipe, but different monomer type, i.e., run 92 with MMA and run 97 with VAC, the effect of the monomer species is obtained. In particular, let us compare the corresponding two curves representing the sound propagation velocity as a function of conversion, shown in Figures 4 and 6, respectively. It can be seen that they are significantly different, and that this difference increases with conversion. This indicates that the values of sound propagation velocity in the two homopolymers are more different than the corresponding values in the two monomers. In principle, this feature could be used to gain informations about the composition in emulsion copolymerization systems based on sound propagation velocity measurements. Finally, note that the overall change of the sound propagation velocity in the case of VAC is lower than that corresponding to MMA, i.e., about 50 vs. 100 m/s for monomer to water ratio equal to about 0.15.

## MODELING OF SOUND PROPAGATION VELOCITY IN EMULSIONS

### Interphase Monomer Partitioning

In order to evaluate the velocity of sound propagation in a multiphase system such as an emulsion, a full characterization of the relative amount and composition of each phase is required. During the emulsion polymerization process in a batch reactor, conversion is defined by:

$$X = \frac{P}{M^0} = \frac{M^0 - M}{M^0} \quad (2)$$

where  $M$  and  $P$  indicate the overall amount of monomer and polymer in the reactor, respectively, and  $M^0$  the amount of monomer initially charged. In general, the reacting system proceeds from a first

stage (Intervals I and II), where monomer is partitioned in three different phases (aqueous solution,  $M_w$ , oil droplets,  $M_D$ , and polymer particles,  $M_p$ ), to a second stage (Interval III) where oil droplets are no longer present, i.e.  $M_D = 0$ . Thus, in the first stage, the overall amount of residual monomer,  $M$  may be expressed as:

$$M = M^0(1 - X) = M_w + M_p + M_D \quad (3)$$

We now proceed to evaluate the amount of monomer in each phase. By introducing the volume fraction of monomer in swollen polymer particles,  $\Phi_m$  the overall amount of monomer in polymer particles,  $M_p$  is given as a function of conversion by:

$$M_p = \frac{\Phi_m}{1 - \Phi_m} \frac{\rho_m}{\rho_p} X M^0. \quad (4)$$

where  $\rho_m$  and  $\rho_p$  represent the density of monomer and polymer in the swollen polymer particles, respectively. On the other hand, the amount of monomer solubilized in the aqueous phase can be evaluated with reasonable accuracy by assuming a linear relationship between the monomer massive concentration in the aqueous phase,  $[M]_w$  and the monomer volume fraction in the polymer particles,  $\Phi_m$ ,<sup>17</sup> i.e.:

$$[M]_w = K_{WP} \Phi_m = \frac{[M]_w^*}{\Phi_m^*} \Phi_m \quad (5)$$

where  $[M]_w^*$  and  $\Phi_m^*$  indicate saturation concentration in aqueous phase and maximum swelling ratio, respectively. Thus, the amount of monomer,  $M_w$  solubilized in the overall amount of aqueous phase,  $W^0$ , is given by  $[M]_w W^0$ . By combining eqs. (3) to (5), the amount of monomer in the oil droplets is obtained:

$$M_D = \left[ 1 - X \left( 1 + \frac{\Phi_m}{1 - \Phi_m} \frac{\rho_m}{\rho_p} \right) \right] M^0 - K_{WP} \Phi_m W^0 \quad (6)$$

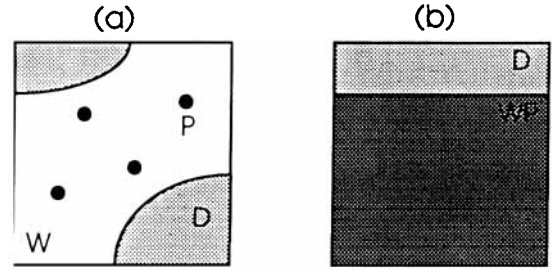
The equations above provide the phase partitioning of the monomer during the entire polymerization process. In particular, in the first stage of the reaction, due to the presence of oil droplets, the polymer particles are saturated by the monomer, i.e.,  $\Phi_m$  and  $\Phi_m^*$ , and the amounts of monomer in polymer particles, aqueous phase, and oil droplets are given as a function of conversion by eqs. (4) to (6), respectively. In the second stage of the reaction, oil droplets are no longer present and the volume frac-

tion of monomer in the polymer particles is smaller than the saturation value, i.e.,  $\Phi_m < \Phi_m^*$ . Thus, for any given conversion value in this stage, the amounts of monomer in aqueous phase and polymer particles are again given by the same equations above, with the exception of  $\Phi_m$ , which is now evaluated through eq. (6), with  $M_D = 0$ . The conversion value corresponding to the transition from one stage to the other,  $\bar{X}$  is obtained from eq. (6) by setting  $M_D = 0$  and  $\Phi_m = \Phi_m^*$  to yield:

$$\bar{X} = \frac{1 - [M]_w^* W^0 / M^0}{1 + (\rho_m / \rho_p) \Phi_m^* / (1 - \Phi_m^*)} \quad (7)$$

### Ultrasound Propagation Velocity in Dispersed Systems

The theoretical evaluation of the sound propagation velocity in dispersed systems, such as suspensions and emulsions, is widely discussed in the literature.<sup>18-21</sup> An important parameter is the ratio between the size of the dispersed particles,  $d$  and the wavelength of the sound wave,  $\lambda$ . In the system under examination we have two dispersed phases: oil droplets ( $D$ ) and polymer particles ( $P$ ), which are characterized by largely different diameter values,  $d_D \simeq 10 \mu\text{m}$  (initial value) and  $d_P \simeq 0.1 \mu\text{m}$  (final value), respectively. The value of the sonic wavelength in water corresponding to a frequency of 3 MHz is about  $\lambda = 500 \mu\text{m}$ . Thus, a generic elemental volume of the emulsion with cubical shape and size  $\lambda/10$  contains typically about 30 oil droplets and three  $10^7$  polymer particles (note that these values correspond to a monomer to water ratio equal to 0.15 and the initial and final sizes indicated above). Following the analysis of Ahuja,<sup>20</sup> we can conclude that in the system water-polymer particles, the latter are so small that we can regard the dispersion as a single phase. Indeed, the velocity of sound in such a system is affected by the presence of polymer particles, as we will discuss later in detail. On the other hand, the same conclusion does not apply to the case of oil droplets. In this case, due to the low number of large particles inside the elemental volume of emulsion, the system has been described as completely segregated, i.e., the oil droplets size is too large to affect the sound propagation. Accordingly, we can calculate the sound propagation velocity in the emulsion by regarding it as constituted of two phases, segregated as shown in Figure 7: the first one is the homogeneous mixture of water and polymer particles ( $WP$ ), and the second one is constituted by the oil droplets ( $D$ ).



**Figure 7** Schematic representation of the emulsion. (a) the real system and (b) the equivalent two-phase segregated system.  $D$  = oil droplets,  $P$  = polymer particles,  $W$  = aqueous phase,  $WP$  = homogeneous mixture of aqueous phase and polymer particles.

Two different equations for sound velocity estimation have been adopted, corresponding to the two extreme situations identified above: dispersion of extremely small particles, and complete segregation.

Let us first estimate the sound propagation velocity in the homogeneous mixture of water and polymer particles  $WP$ , following the relation proposed by Ahuja:<sup>20</sup>

$$v_{WP}^2 = v_W^2 \frac{1 - \phi L \cos \epsilon}{[1 - \phi(1 - \beta_P / \beta_W)][1 + \phi L(\tau \cos \epsilon + s \sin \epsilon)]} \quad (8)$$

where  $v_{WP}$  and  $v_W$  indicate the sound propagation velocity in phase  $WP$  and in water, respectively,  $\phi$  is the fractional volume of particles in the water-particle system, and  $\beta$  the compressibility. The remaining variables are expressed as follows:

$$L = \frac{\rho_P / \rho_W - 1}{[(\rho_P / \rho_W + \tau)^2 + s^2]^{1/2}}; \quad \epsilon = \tan^{-1} \frac{s}{\rho_P / \rho_W + \tau} \quad (9)$$

$$\tau = \frac{1}{2} + \frac{\delta}{4r_P} \frac{(2\eta_W + 3\eta_P)^2}{(\eta_W + \eta_P + r_P \eta_W / 3\delta)^2 + (r_P \eta_W / 3\delta)^2} \quad (10)$$

$$s = \frac{3\delta^2}{4r_P^2} (2\eta_W + 3\eta_P) \times \frac{(1 + r_P / \delta)(\eta_W + \eta_P + r_P \eta_W / 3\delta) + \eta_W r_P^2 / 3\delta^2}{(\eta_W + \eta_P + r_P \eta_W / 3\delta)^2 + (\eta_W r_P / 3\delta)^2} \quad (11)$$

where  $r_P$  indicates the average particle radius,  $\eta$  the viscosity of the aqueous phase ( $\eta_W$ ) and the polymer

particles ( $\eta_P$ ),  $\delta = (2\eta_W/\rho_W\omega)^{0.5} = 3 \cdot 10^{-5}$  cm, being  $\omega$  the angular frequency of the sonic wave and  $\rho_P (= (M_P + P)/(M_P/\rho_m + P/\rho_p))$  the density of the polymer particles.

The equations above can be substantially simplified by introducing the following assumptions: (1) the viscosity of the polymer particle is much larger than that of the aqueous phase, i.e.,  $\eta_P \gg \eta_W$ ; (2) the dimensionless quantity  $L$ , defined by eq. (9), approaches zero. While the first assumption may be easily understood, the second one requires some analysis. By considering the values of the particle radius,  $r_P$  and of the parameter  $\delta$  reported above, it is easily verified that, for the ultrasonic waves considered here, the ratio  $r_P/\delta$  is always less than one. Combining this observation with the assumption  $\eta_P \gg \eta_W$ , the equations for  $\tau$  and  $s$  reduce to:

$$\tau = \frac{1}{2} \left( 1 + \frac{9\delta}{2r_P} \right); \quad s = \frac{9\delta^2}{4r_P^2} \left( 1 + \frac{r_P}{\delta} \right) \quad (12)$$

Substituting these relations in eqs. (9) and noting that  $s \gg \tau$ , the following expressions for  $L$  and  $\epsilon$  are obtained:

$$L = \frac{\rho_P/\rho_W - 1}{s}; \quad \epsilon = \frac{\pi}{2} \quad (13)$$

and eq. (8) can be simplified as follows:

$$v_{WP}^2 = v_W^2 \frac{1}{[1 - \phi(1 - \beta_P/\beta_W)][1 - \phi(1 - \rho_P/\rho_W)]} \quad (14)$$

It is worth pointing out that the equation above involves only the values of compressibility, volume ratio of the dispersed phase, and sound velocity in the aqueous phase. Quantities such as particle viscosity and size are no longer involved, thus making significantly easier the application of this equation. Thus, summarizing, eq. (14) provides the sound propagation velocity,  $v_{WP}$  in a dispersion where the size of the dispersed particles is smaller than the parameter  $\delta$ , i.e.,  $r_P/\delta \ll 1$ , and the viscosity of the particles is larger than that of the continuous phase, i.e.,  $\eta_P \gg \eta_W$ .

Let us now consider the segregated system constituted by the two phase  $WP$  and  $D$ . In this case a simple equation, proposed by Bonnet and Tavlarides<sup>22</sup> in the context of liquid-liquid dispersions, has been used. Accordingly, the sound velocity in the emulsion,  $v_E$  is related to the sound velocities in the two phases by:

$$\frac{1}{v_E} = \frac{\Phi_D}{v_D} + \frac{\Phi_{WP}}{v_{WP}} \quad (15)$$

where  $\Phi_D$  and  $\Phi_{WP}$  indicate the volume fractions of the two phases.

In order to use the equations above for estimating  $v_E$ , it is necessary to properly evaluate all the involved parameters. In particular, those related to the polymer particles change continuously during the polymerization reaction. This can be accounted for through the equations derived in the previous section, which allow us to represent the parameters  $\Phi_D$ ,  $\Phi_{WP}$ ,  $\phi$ , and  $\beta_P$  in eqs. (14) and (15) as a function of conversion as follows:

$$\Phi_D = \frac{M_D/\rho_m}{V_E}, \quad \Phi_{WP} = 1 - \Phi_D \quad (16)$$

$$\phi = \frac{V_P}{W^0/\rho_W + M_W/\rho_m + V_P}, \quad V_P = \frac{M_P}{\rho_m} + \frac{P}{\rho_p} \quad (17)$$

$$\beta_P = \beta_m \Phi_m + \beta_p(1 - \Phi_m) \quad (18)$$

where:

$$V_E = \frac{M_D + M_P + M_W}{\rho_m} + \frac{P}{\rho_p} + \frac{W^0}{\rho_W} \quad (19)$$

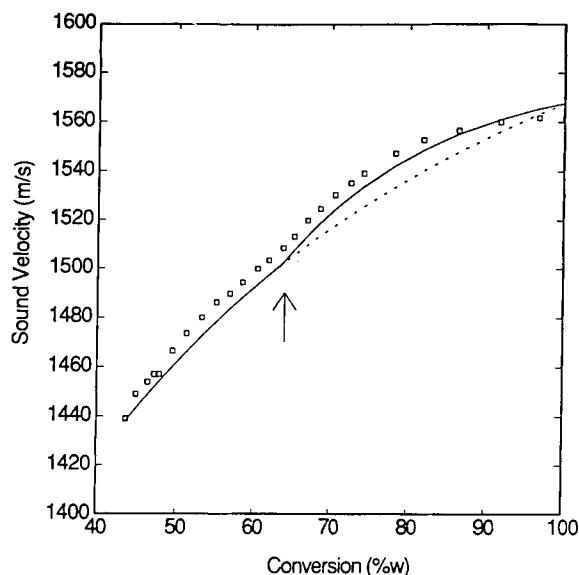
$$\beta_W = \frac{1}{v_W^2 \rho_W}, \quad \beta_m = \frac{1}{v_m^2 \rho_m}, \quad \beta_p = \frac{1}{v_p^2 \rho_p}. \quad (20)$$

It can be seen in the equations above that the volume additivity rule has been used, while the compressibility of the polymer particle has been computed in eq. (18) through a linear volume average.<sup>23</sup> This relation is, indeed, the most critical, particularly as the polymerization proceeds and the polymer to monomer ratio increases. It is known that, as the concentration of polymer chains increases, significant changes in the transport properties of the polymer particles occur.<sup>24</sup> For example, this is the case of viscosity, which increases at high polymer concentrations, thus reducing the mobility of the growing radical chains inside the particle. This is known as *gel effect*, and has the important implication with respect to the kinetics of the polymerization process of reducing the termination and, to a minor extent, the propagation reaction rates.<sup>25</sup> Actually, while the mobility of the active chains reduces continuously from low to high conversion, the mobility of monomer is significantly reduced only when the polymeric matrix undergoes a drastic change corresponding to a phase transition. This happens when the monomer



to polymer ratio is such that the reaction temperature becomes equal to the glass transition temperature,  $T_g$  of the mixture. At this point, the polymerization reaction practically stops.

Similarly to viscosity, the occurrence of interactions or entanglements among polymeric chains affects also the compressibility of the particle and, therefore, the propagation of sound. To account for this phenomenon, we developed an empirical correlation for the polymer particle compressibility based on independent experimental data, obtained *ad hoc* with a spent latex. In particular, the sound propagation velocity has been measured starting with a spent polyMMA latex ( $W^0 = 678$  g,  $P = 73.3$  g, SLS = 4.5 g) while adding continuously the monomer (MMA), under nonreacting conditions. The measured values of sound propagation velocity,  $v_E$  are shown in Figure 8 as a function of conversion, which, in this case, is given by the ratio between the amounts of polymer and of polymer plus monomer added to the system. In the same figure, the dotted curve represents the model results using the volume average to compute the compressibility of the polymer particle, i.e., eq. (18). The numerical values of model parameters summarized in Table III have been used (a detailed discussion about values and corresponding sources is reported in the next section). It is apparent that the calculated curve does



**Figure 8** Values of sound propagation velocity as a function of conversion obtained by continuously adding monomer to a spent polyMMA latex. □ = experimental data; (---) = model predictions with  $\beta_p$  from eq. (18); (—) = model predictions with  $\beta_p$  from eqs. (18) and (21) with  $\Phi_{cr} = 0.4$ .

**Table III** Numerical Values of Model Parameters ( $T = 50^\circ\text{C}$ )

Parameter	VAC	MMA	Source
$\rho_m$ (g/cm <sup>3</sup> )	0.932	0.919	27
$\rho_p$ (g/cm <sup>3</sup> )	1.170	1.190	27
$\nu_m$ (m/s)	930	1000	Fitting
$\nu_p$ (m/s)	1600	2200	Fitting
$\phi^*$ (cm <sup>3</sup> /cm <sup>3</sup> )	0.85	0.77	30,31
$[M]_w^*$ (g/cm <sup>3</sup> )	0.0234	0.0156	30
$\Phi_{cr}$ (cm <sup>3</sup> /cm <sup>3</sup> )	—	0.40	Fitting

not account for the discontinuity exhibited by the experimental data at the conversion value equal to about 64%. On the other hand, the agreement with the experiments for lower conversion values is satisfactory.

In order to improve the model results in the region of high conversion values, the volume average relation for the polymer particle compressibility eq. (18) has been replaced by the following empirical relationship:

$$\beta_p = \beta_m \Phi'_m + \beta_p (1 - \Phi'_m) \quad (21)$$

where the new quantity  $\Phi'_m$ , a corrected monomer volume fraction, is defined as:

$$\Phi'_m = \Phi_m \frac{1 - \Phi_{cr}}{1 - \Phi_m} \quad (22)$$

Equation (21) has been designed in order to modify the linear average given by eq. (18) by increasing the weight of the polymer compressibility with respect to that of the monomer. It applies for monomer volume fractions in the polymer particles,  $\Phi_m$  smaller than a critical value,  $\Phi_{cr}$  which represents the onset of significant interactions among the polymer chains and then the deviation from the linear volume average relation for computing the compressibility. Note that  $\Phi_{cr}$  is the only adjustable parameter present in eq. (21). Moreover, the same equation satisfies correctly the limiting conditions: the value of  $\beta_p$  calculated when  $\Phi_m = \Phi_{cr}$  is the same as that predicted by eq. (18) and  $\beta_p = \beta_p$  when  $\Phi_m = 0$ . For example, in the case of MMA, illustrated in Figure 8, the critical value  $\Phi_{cr} = 0.40$  corresponds to a conversion of about 64%. Using the value reported above, the continuous curve shown in Figure 8 has been obtained, which provides a reasonable description of the experimental data.

It is worth noting that in the case of VAC no transition has been evidenced during the polymer-

ization reaction. Thus, for VAC, the linear volume average relation (18) has been used for calculating the polymer particle compressibility throughout the entire process.

### Comparison with Experimental Data

The proposed model has been validated by comparison with the experimental data shown in Figures 4 and 6 for MMA and VAC, respectively. An important aspect of such a comparison is the evaluation of the model parameters. The values of the parameters relative to the aqueous phase at 50°C have been taken from the literature:  $\rho_w = 0.988 \text{ g/cm}^3$  and  $v_w = 1542.9 \text{ m/s}$ .<sup>26</sup> For monomer and polymer species, the corresponding values are summarized in Table III. The value of sound propagation velocity in the monomer,  $v_m$ , has been estimated so as to reproduce the experimental value of the initial  $v_E$ , which, since the polymer is absent, depends only on  $v_m$ . On the other hand, the sound speed in polymer,  $v_p$  and the critical monomer volume fraction in particle,  $\Phi_{cr}$  have been estimated by fitting the experimental data discussed in the last section. Note that the  $v_p$  value for polyMMA is in close agreement with that taken from the Polymer Handbook,<sup>27</sup> and that this lies between the two values corresponding to longitudinal ( $v_{pl}$ ) and shear ( $v_{ps}$ ) sound propagation modes in the pure solid polymer ( $v_{pl} = 2690 \text{ m/s}$ ;  $v_{ps} = 1340 \text{ m/s}$ ;<sup>28</sup>). In the case of polyVAC, no experimental value of  $v_p$  has been found in the literature. However, the estimated value is within the range  $v_{pl}-v_{ps}$  as calculated by the group contribution method<sup>29</sup> ( $v_{pl} = 1830 \text{ m/s}$ ;  $v_{ps} = 730 \text{ m/s}$ ).

A comparison between model and experimental results in the case of MMA is shown in Figure 9. The same data shown earlier in Figure 4 have been compared in Figure 9(a) with the calculated curves as obtained through the model (broken curves) using the parameter values discussed above. The calculated curves are shown alone in Figure 9(b) in order to evidence two discontinuities. The first one corresponds to the disappearance of the oil droplets, while the second one reflects the polymer phase transition occurring at  $\Phi_{cr}$ . The agreement between model and experimental results is satisfactory.

A similar result has been obtained in the case of VAC. The same data of Figure 6 have been compared in Figure 10(a) with the calculated curve. Note that three sets of experimental data but only one model calculation are shown, due to the observed negligible effect of emulsifier and initiator concentrations on the sound propagation velocity in the emulsion. As in the case of MMA, the calculated curve is shown

alone in Figure 10(b). It is apparent that for this system only one discontinuity point arises, i.e., the one related to the oil droplet disappearance, because no polymer phase transition has been considered in the model.

### ASSESSMENT OF THE ON-LINE CONVERSION SENSOR

In the following, two calibration procedures for using the sound velocity sensor to estimate monomer conversion values are considered. The first one is empirical. It is based on a preliminary polymerization run used to derive the sound propagation velocity vs. conversion calibration curve, while no model is required. The second procedure is based on the model developed in the previous section, which relates the velocity of sound propagation in the emulsion to its physico-chemical properties, including conversion. It does not require any calibration reaction but, rather, the evaluation of all involved parameters such as densities, compressibilities, and sound propagation velocities in all components.

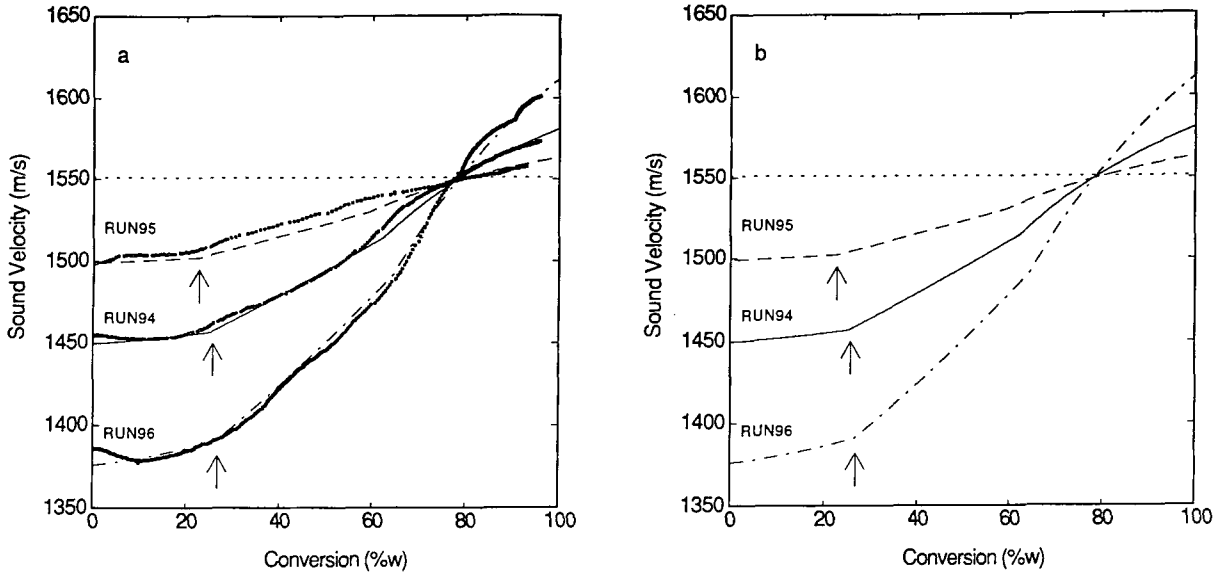
#### Empirical Calibration Procedure

A preliminary polymerization reaction is performed and sound velocity data measured on line, together with conversion data measured off line, are collected. From these, the experimental calibration curve is extracted, i.e., a sound propagation velocity vs. conversion master curve is constructed. Now, starting from the subsequent reaction, it is possible, using this calibration curve, to obtain on-line conversion data from the measured sound velocity values.

From the results discussed in the previous section, we expect the calibration curve to be substantially independent of recipe variations involving the emulsifier and initiator concentrations. On the other hand, if the monomer to water ratio is modified, a new calibration curve should be derived. However, this can be avoided by using the following empirical rule for scaling the effect of different monomer to water ratios. In particular, the sound velocity in the emulsion,  $v_E$  when the value  $M^0/W^0$  is different from that of the calibration run,  $(M^0/W^0)_{ref}$ , can be evaluated as:

$$v_E = (v_{E,ref} - v_w) \frac{M^0/W^0}{(M^0/W^0)_{ref}} + v_w \quad (23)$$

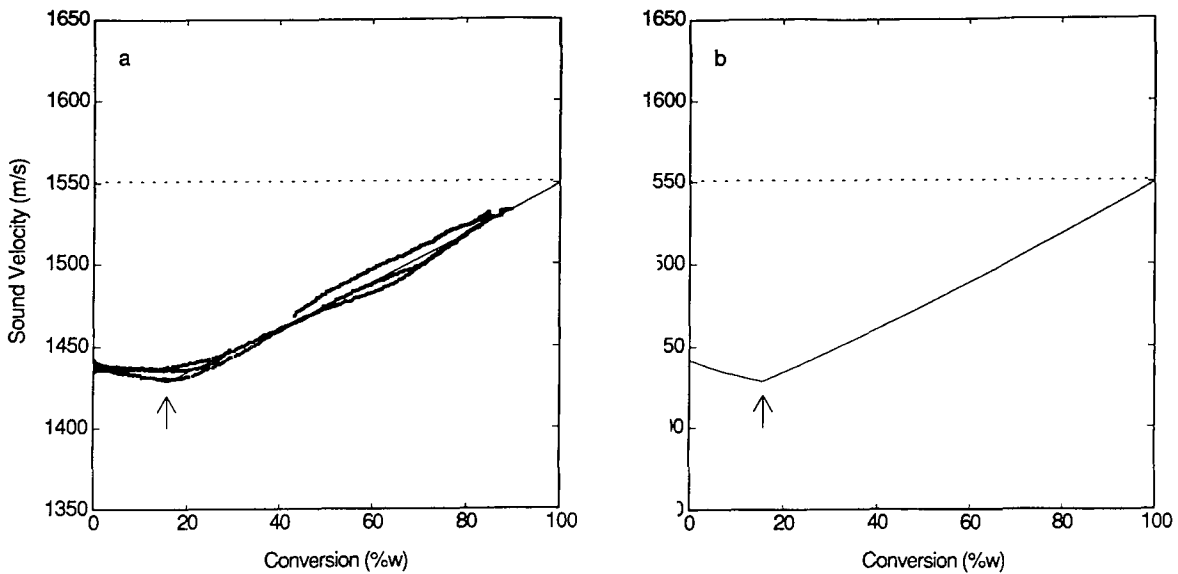
where  $v_{E,ref}$  indicates the sound speed evaluated through the original experimental calibration curve.



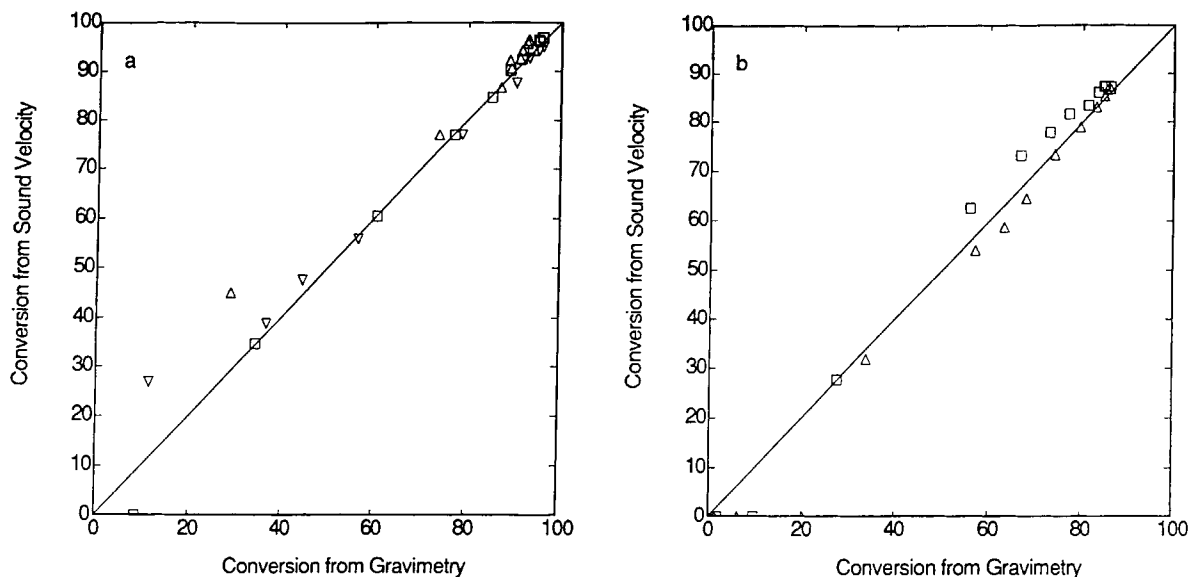
**Figure 9** (a) Comparison between measured sound velocity data and model predictions for runs 94, 95, and 96. (b) Calculated curves. The arrows indicate the disappearance of oil droplets.

As an example of application of this procedure, let us reconsider the experimental data for both MMA and VAC. The runs 92 and 97 are used as calibration run and the corresponding calibration curve is applied to estimate conversion for all the remaining experiments (runs 94, 95, and 96 for MMA; runs 98 and 99 for VAC). The estimated conversion values are compared with those measured

off line through gravimetry for the two systems in Figure 11(a) and (b). The obtained agreement is satisfactory. Significant errors are evidenced at low conversion values (less than 40%) in Figure 11(a) for MMA. These may be due to the empirical correction given by eq. (23), whose accuracy increases with the amount of produced polymer. It is worth noting that this empirical calibration procedure can



**Figure 10** (a) Comparison between measured sound velocity data and model predictions for runs 97, 98, and 99. (b) Calculated curves. The arrows indicate the disappearance of oil droplets.



**Figure 11** Comparison between conversion values estimated on-line from sound velocity measurements and measured off-line through gravimetry. Empirical calibration procedure. (a)  $\square$  = run 94,  $\triangle$  = run 95, and  $\nabla$  = run 96; calibration based on run 92. (b)  $\square$  = run 98 and  $\triangle$  = run 99; calibration based on run 97.

be useful in industrial applications where constant reaction conditions are maintained in subsequent batches so as to guarantee products with uniform characteristics.

### Model-Based Calibration Procedure

In this case, the conversion value is calculated from the measured sound propagation velocity using the model developed in the previous section, thus avoiding any experimental calibration run while requiring some preliminary experiments to estimate the model parameters.

A comparison between conversion data measured off line through gravimetry and the corresponding values obtained using the sound speed model is shown in Figure 12, with reference to the same experiments shown in Figure 11 in addition to the two reactions that were used as calibration runs. A good agreement is evidenced in all cases, thus confirming the model reliability. It appears that some inaccuracies arise at low conversion values, as in the case of the empirical calibration procedure. This failure, which is common to both the examined calibration procedures for conversion monitoring, reflects the weak sensitivity of the sensor when droplets are present and constitutes a limitation of the developed technique, at least in its present form.

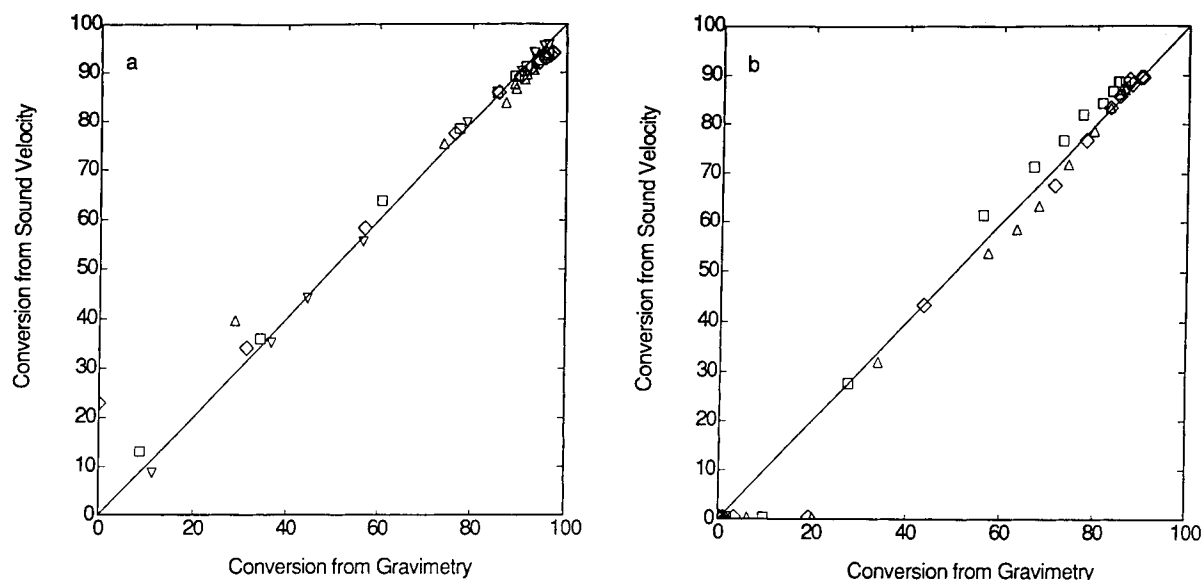
### CONCLUSIONS

In this work, an on-line conversion sensor, based on the measurement of the velocity of sound propagation in the emulsion is developed. The sensor is particularly suited for applications in industrial environments, because it does not require the installation of a sampling circuit, but it can be directly plugged in the reacting mixture. The reliability of the on-line sensor has been tested, by comparison with off-line gravimetric measurements of conversion, for the homopolymerization of methyl methacrylate and vinyl acetate under various operating conditions. The sound propagation velocity vs. the conversion calibration curve can be obtained experimentally through a preliminary polymerization run. Alternatively, the calibration curve can be calculated *a priori*, using a model specifically developed for this purpose.

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### NOMENCLATURE

$d_D$  = oil droplet diameter, cm  
 $d_P$  = polymer particle diameter, cm



**Figure 12** Comparison between conversion values estimated on-line from sound velocity measurements and measured off-line through gravimetry. Model based calibration procedure. (a)  $\diamond$  = run 92,  $\square$  = run 94,  $\triangle$  = run 95, and  $\nabla$  = run 96. (b)  $\diamond$  = run 97,  $\square$  = run 98, and  $\triangle$  = run 99.

$K_{WP}$  = monomer partition coefficient between polymer particles and water,  $g/cm^3$

$L$  = distance between transducers, mm

$M$  = overall amount of monomer in the reactor, g

$M_D$  = amount of monomer in oil droplets, g

$M_P$  = amount of monomer in polymer particles, g

$M_W$  = amount of monomer in aqueous solution, g

$[M]_W$  = monomer massive concentration in aqueous solution,  $g/cm^3$

$[M]_W^*$  = monomer massive concentration in aqueous solution at saturation,  $g/cm^3$

$P$  = amount of polymer in the reactor, g

$r_p$  = polymer particle radius, cm

$s$  = parameter defined by eq. (11)

$T$  = temperature, C

$T_g$  = glass transition temperature, C

$v_E$  = sound propagation velocity in emulsion, m/s

$v_W$  = sound propagation velocity in aqueous solution, m/s

$v_{WP}$  = sound propagation velocity in phase PW, m/s

$v_m$  = sound propagation velocity in pure monomer, m/s

$v_p$  = sound propagation velocity in pure polymer, m/s

$W^0$  = amount of water in the reactor, g

$X$  = conversion defined by eq. (2)

$\bar{X}$  = conversion value corresponding to oil droplet disappearance, given by eq. (7)

### Greek Letters

$\alpha$  = constant factor in eq. (1), m/s C

$\beta_m$  = compressibility modulus of pure monomer,  $s^2m/kg$

$\beta_p$  = compressibility modulus of pure polymer,  $s^2m/kg$

$\beta_P$  = compressibility modulus of polymer particles,  $s^2m/kg$

$\beta_W$  = compressibility modulus of aqueous phase,  $s^2m/kg$

$\delta = 2\eta_W/(\rho_w\omega)$

$\epsilon$  = parameter defined by the second of eqs. (9)

$\eta_P$  = polymer particle viscosity,  $g/cm^3s$

$\eta_W$  = aqueous phase viscosity,  $g/cm^3s$

$\lambda$  = ultrasound wavelength, cm

$\rho_m$  = density of pure monomer,  $g/cm^3$

$\rho_P$  = density of pure polymer,  $g/cm^3$

$\rho_P$  = density of the polymer particles,  $g/cm^3$

$\rho_w$  = density of aqueous phase,  $g/cm^3$

$\phi$  = fractional volume of particles in the water particle system

$\Phi_{cr}$  = critical volume fraction of monomer in particle

- $\Phi_m$  = volume fraction of monomer in particle  
 $\Phi'_m$  = corrected volume fraction of monomer in particle, defined by eq. (22)  
 $\Phi_m^*$  = saturation volume fraction of monomer in particle  
 $\Phi_D$  = volume fraction of oil droplets in the emulsion  
 $\Phi_{WP}$  = volume fraction of phase WP in the emulsion  
 $\omega$  = angular frequency of the ultrasonic wave

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