Procedure for Calibrating an Ultrasonic Sensor for Online Monitoring of Conversion in Latex Reactors

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ABSTRACT: In order to estimate online conversion and polymer composition through sound velocity measurements, a mathematical model for calculating sound velocity in emulsion polymerization has been developed. With respect to previous modeling approaches, its main features are as follows: (1) the application to three-phase, reacting systems of Urick equation (usually adopted for estimating sound velocity in multiphase, dispersed, unreacting systems, such as emulsions and suspensions); and (2) the development of an empirical relationship for estimating particle compressibility as a function of conversion during the reaction. The model has been validated through several sets of experimental data of batch and semibatch homo- and copolymerizations involving styrene, butyl acrylate, vinyl acetate, and methyl methacrylate. In most of the examined cases, the performances of the calibration model are satisfactory. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1451–1477, 1999

Key words: emulsion polymerization; online monitoring; ultrasonics; latex reactors

INTRODUCTION

An important aspect in the quality control of polymers produced in polymerization reactors is the online monitoring of the state of the system in terms of product properties, besides the usual reactor conditions, such as temperature and pressure. With this respect, a relevant amount of work has been devoted to the development of online sensors, mostly aimed to monitor conversion and copolymer composition (cf. review articles^{1,2}). In the case of emulsion homopolymerizations, excellent results have been reported when using a sensor based on the measurement of the sound propagation velocity in the reacting system.^{3,4} The main advantages of such a sensor are easy installation, general robustness, limited cost, and the absence of sampling devices since the measurement is obtained in situ without disturbing the system evolution. On the other hand, such sensors need appropriate calibration. Both empirical and model-based calibration procedures have been developed for the case of homopolymerization. In this work, we reconsider the calibration problem in a more comprehensive way. Namely, we develop a simpler and more reliable calibration procedure, and we extend it to the case of different reactor operating modes (batch and semibatch) and multimonomer systems. As we will see, the new calibration procedure requires, at most, to run a preliminary batch polymerization reaction.

The outline of this article is as follows. After a short description of the experimental arrangement and materials, a model for evaluating the sound propagation velocity in the multiphase, dis-

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Figure 1 Scheme of the experimental apparatus.

persed systems typical of emulsion polymerization reactors is presented. Based on this model, a calibration procedure is developed, which requires a single batch reaction for each different polymerization system. Namely, this single experiment provides an efficient estimate of all the adjustable model parameters. Finally, the reliability of the proposed calibration procedure is demonstrated by comparison with a large set of experimental data. Monitoring of conversion in homo- and copolymerization systems in batch and semibatch operating modes is presented.

EXPERIMENTAL APPARATUS AND MATERIALS

The adopted experimental apparatus has been described in detail,⁴ and it is schematically shown in Figure 1. The 2-L volume, glass reactor (1) is equipped with baffles, stirrer, and condenser. The ultrasonic probe (2) and the thermocouple (3) are plugged into the reactor through its cover. The sensor is constituted by two piezoelectric crystals, one emitter and one receiver. The frequency of the sonic pulse is 1.5 MHz. Sound velocity and atten-

uation data are simultaneously collected by the sensor. Temperature control is performed by flowing water through the reactor jacket; water temperature is controlled by a thermostatic bath (4). The electric signals of thermostatic bath, thermocouple, and ultrasonic sensor are sent to a PC (6) equipped with a specifically designed interface (5), connected to the parallel port of the computer. To operate the reactor in semibatch mode, two dosing pumps (7 and 8) are used. They are connected to the computer, which supervises their operation, through the serial port. About chemicals, water has been deionized and distilled before use while monomers [methyl methacrylate (MMA), vinyl acetate (VAc), styrene (Sty), and butyl acrylate, (BuA)], emulsifier (sodium lauryl sulfate), and initiator (potassium or sodium persulphate), have been used as received (from Fluka) without further purification.

MODELING OF SOUND PROPAGATION VELOCITY

Sound Velocity in Dispersed Systems

In single-phase, single-component systems, the velocity of an ultrasonic wave is related to the

physical properties of the medium through the following equation:

$$C = \sqrt{\frac{\epsilon}{\rho}} \tag{1}$$

where ρ indicates the phase density, and ϵ is the appropriate elastic modulus. While in solids, ultrasound waves propagate in compressional and shear waves, in fluid, they reduce to compressional waves only due to the strong absorption of the shear components. In this second case, the appropriate elastic modulus is the reciprocal of the adiabatic compressibility β , defined as $-1/V(\partial V/\partial P)_s$, and eq. (1) becomes

$$C = \frac{1}{\sqrt{\rho\beta}} \tag{2}$$

Note that when the density value is known, this equation represents a one-to-one relation between sound velocity and compressibility of the pure component. Thus, C and β are often used as equivalent quantities.

In the case of mixtures, composition affects both density and compressibility, and a model relating the properties of the pure components to the corresponding values in the mixture is needed. When dealing with ideal mixtures with N_c components, the following expressions can be used:

$$\rho = \sum_{i=1}^{N_c} \rho_i \phi_i \tag{3}$$

$$\beta = \sum_{i=1}^{N_c} \beta_i \phi_i \tag{4}$$

where ϕ_i indicates the concentration of the *i*th component in the mixture in terms of volume fraction. Note that the first equation is compatible with the simple volume additivity rule, usually adopted in the case of mixtures of chemically similar components.

In dispersed systems, particles or droplets are suspended in a continuous phase, that is, the aqueous matrix in the case of latex reactors. The behavior of ultrasonic waves travelling through such a medium is affected not only by the properties of each phase but also by their relative amounts and by the degree of dispersion, that is,

the particle size of the dispersed phase. A detailed theoretical description of the behavior of ultrasonic waves in dispersed systems has been developed in the frame of the scattering theory by Epstein and Carhart⁵ for liquid droplets and extended to solid particles by Allegra and Hawley.⁶ Accordingly, sound velocity and attenuation (that is, the total energy loss by the travelling wave due to various dissipation mechanisms) are function of frequency, particle size, and several physical quantities of both continuous and dispersed phases, such as density, compressibility, heat capacity, thermal conductivity, and intrinsic attenuation. The resulting expression is complex, and the evaluation of all the involved parameters is not a trivial task. However, as shown by Mc-Clements and Povey,⁷ the relevance of scattering on sound velocity and attenuation is completely different and much larger in the second case. Thus, when modeling only sound velocity alternative, simpler approaches, valid for nonscattering systems, can be considered. Note that this conclusion is limited to relatively dilute systems (about 20% of volume fraction of dispersed phase) and to the so called Long-Wavelength Regime (LWR),⁶ that is, sound wavelengths larger than the particle size of the dispersed phase. This last requirement is indeed fulfilled in the case of latex reactors with respect to both monomer droplets and polymer particles when dealing with sound frequency values of the order of 1 MHz, like in the case of the sensor under examination here.

An effective, empirical model has been proposed by Urick⁸ for two-phase, dispersed systems. When extended to multiphase systems, this model gives an expression for the sound speed in the dispersion which is identical to eq. (2) for homogeneous systems; that is,

$$C = \frac{1}{\sqrt{\rho_e \beta_e}} \tag{5}$$

but now effective values of both density and compressibility, referring to the dispersion as a whole, are present. Their evaluation may be performed as follows:

$$\rho_e = \sum_{i=1}^{N} \rho_i \Phi_i \tag{6}$$

$$\beta_e = \sum_{i=1}^{N} \beta_i \Phi_i \tag{7}$$

where N indicates the number of involved phases, and Φ is the volume fraction of each phase. Since the involved density and compressibility values are those of the pure phases, eq. (5) predicts that sound velocity is independent of both sound wave frequency and particle size. Despite its simplicity, and under the limitations stated above, the previous equation gives satisfactory predictions in both liquid and solid dispersed systems. Note that density and compressibility values in the righthand side of eqs. (6) and (7) can be computed, in the case of ideal mixtures, through eqs. (3) and (4). More complex expressions are required for nonideal systems.

Sound Velocity in Emulsion Polymerization Systems

A typical emulsion polymerization is performed in a three-phase system constituted of water, the continuous phase, monomer droplets, the only dispersed phase present at the beginning of the reaction, and polymer colloidal particles, the final product. Other additives like initiator, emulsifiers, activator, and chain transfer agent are usually present at a negligible extent from the sound propagation view point. In fact, preliminary experiments with and without them^{3,9} confirmed that the presence of typical amounts of such additives does not affect sound velocity in the system. Thus, the velocity of sound propagation in a latex reactor is a function of relative amounts and physical properties of water, monomer, and polymer phases.

As mentioned in the Experimental Apparatus and Materials section the frequency of the sound waves here considered is 1.5 MHz. This means that the corresponding wavelength in water is about 1.5 10^{-3} m, then much larger than the typical sizes of both the dispersed phases, that is, monomer droplets (about 10 μ m) and polymer particles (about 0.1 μ m). Thus, the essential requirement for LWR is well fulfilled. Moreover, as discussed later in more detail, reactions with limited monomer-to-water ratio have been considered so as to fulfill the second requirement for nonscattering system and to justify the use of eqs. (5) to (7) to calculate the sound speed.

Let us now examine how to apply these equations to the particular system of interest here. According to eqs. (6) and (7), the effective density and compressibility for a polymer latex containing monomer droplets are given by

$$\rho_e = \Phi_d \rho_d + \Phi_{\text{par}} \rho_{\text{par}} + (1 - \Phi_d - \Phi_{\text{par}}) \rho_{aq} \quad (8)$$

$$\beta_e = \Phi_d \beta_d + \Phi_{\text{par}} \beta_{\text{par}} + (1 - \Phi_d - \Phi_{\text{par}}) \beta_{aq} \quad (9)$$

where Φ_d and Φ_{par} indicate the total volume fractions of droplets and particles, respectively. Substituting in eq. (5), the following expression for the sound velocity C_e in the three-phase system is obtained:

$$C_{e}^{2} = \frac{C_{aq}^{2}}{\left[1 - \Phi_{d}(1 - \rho_{d}/\rho_{aq}) - \Phi_{\text{par}}(1 - \rho_{\text{par}}/\rho_{aq})\right]} \\ \left[1 - \Phi_{d}(1 - \beta_{d}/\beta_{aq}) - \Phi_{\text{par}}(1 - \beta_{\text{par}}/\beta_{aq})\right]$$
(10)

where C_{aq} indicates the sound speed in the aqueous phase. The correct use of eq. (10) requires a careful evaluation of all involved quantities and, in particular, of density and compressibility of the various phases in the system.

Aqueous Phase

Since all minor ingredients, such as initiator, activator, and so on have been neglected, the aqueous phase can be regarded as composed of water and solubilized monomers. Often, monomers exhibit poor solubility in water. In these cases, it may be reasonably assumed that the sonic behavior of the aqueous solution is very similar to that of pure water. As a consequence, the speed of sound, C_{aq} , is considered equal to that of water, C_{w} . Sound speed measurements performed on aqueous solutions of monomers with different water solubilities (MMA, VAc, Sty, and BuA) support this assumption.⁹ About density and compressibility, the same approximation has been adopted, thus using the values of pure water for both ρ_{aq} and β_{aq} . This is consistent with the previous choice $C_{aq} \simeq C_w$. In the case of monomers exhibiting larger water solubilities, it is convenient to compute the mixture density and compressibility as a function of composition using an appropriate equation of state. For ideal mixtures, eqs. (3) and (4) can be used. From these, the velocity of sound propagation can then be computed using eq. (2).

Monomer Droplets

At least for the systems considered in this work, the monomer species are chemically similar so that we can assume that their mixtures exhibit ideal behavior at all composition values. This is the same assumption usually adopted to describe the interphase monomer partitioning in those



Figure 2 Attenuation versus conversion data. Batch homopolymerization: (\diamond) MMA; (\Box) Sty; (\triangle) VAc; (*) BuA.

systems see Schoonbrood et al.¹⁰ Thus, with reference to droplets containing N_m monomer species, eqs. (3) and (4) can be used.

$$\rho_d = \sum_{i=1}^{N_m} \rho_{mi} \phi_{di} \tag{11}$$

$$\beta_d = \sum_{i=1}^{N_m} \beta_{mi} \phi_{di} \tag{12}$$

where ϕ_{di} indicates the volume fraction of monomer *i* in the droplets, and ρ_{mi} and β_{mi} are the density and compressibility of the same pure component, respectively.

Polymer Particles

In emulsion polymerization, the growing particle can be regarded as a microreactor. It is constituted of polymeric chains (growing and terminated) and monomers, continuously supplied by the droplets (as long as they are present) by diffusion through the aqueous phase. Thus, the particle can be regarded as a polymer-monomer mixture whose composition may change along the reaction. In general, nonideal interactions between polymer and monomers prevail, and the ideal equations (3) and (4) cannot be used (cf. the classical thermodynamic treatment by Flory and Huggins¹¹). In other words, a property of the mixture cannot be estimated as a simple volume average of the same property of the pure components. An additional complication is represented by the behavior of the polymer itself, which may undergo the glass phase transition resulting in a significant change of the polymeric matrix behavior, in particular from the mechanical viewpoint.¹² The presence of solubilized monomer affects the glass transition temperature T_g as follows: the larger the monomer concentration, the lower the glass transition temperature of the polymeric matrix. Thus, the glass transition temperature of the polymer phase in the particles increases with conversion as the reaction proceeds. If the reaction temperature is larger than the glass transition temperature during the entire reaction, then no phase transition takes place. However, when the T_g becomes larger than the reaction temperature, this transition takes place. This typically happens at high conversion values and is evidenced by a large drop in the reaction rate due to the loss of mobility of monomers in the glassy polymer, which practically leads to the end of reaction (the so-called limiting $conversion^{13}$).

Let us now develop a model describing the evolution of density and compressibility of a polymer mixture with composition, which accounts for the complex phenomena mentioned above. For this, we have adopted an empirical approach based on the concept of best exploiting all available experimental informations.

In particular, eq. (3) is used for calculating particle density in a multimonomer system, as follows:

$$\rho_{\rm par} = \sum_{i=1}^{N_m} \rho_{mi} \phi_{mi} + \rho_p \phi_p \tag{13}$$

where ϕ_{mi} and ϕ_p indicate the volume fraction of each monomer and of the polymer in the particle, respectively. The copolymer density ρ_p depends upon its composition. This can be accounted for again using a simple volume average,¹⁴ as follows:

$$\rho_p = \sum_{i=1}^{N_m} \rho_{pi} \phi_{pi} / \phi_p \tag{14}$$

where ϕ_{pi} indicates the volume fraction of monomer *i* reacted to copolymer, that is, the copolymer volumetric composition.

In the case of compressibility, eq. (4) has been empirically modified as follows. The mixture compressibility is computed as the sum of the following two contributions: (1) the ideal one, β_{par}^{id} , given by eq. (4); and (2) the nonideal one, $\Delta\beta_{par}$, which accounts for interactions between the polymeric matrix and the monomer species. Moreover, the resulting quantity is multiplied by a correction factor *T* related to the possible occurrence of phase transitions. The final relationship is given by

$$\beta_{\text{par}} = \left[\left(\sum_{i=1}^{N_m} \beta_{mi} \phi_{mi} + \beta_p \phi_p \right) + \Delta \beta_{\text{par}} \right] T \quad (15)$$

The empiricism of the model is in the evaluation of the parameters T, $\Delta\beta_{par}$, and the polymer compressibility, β_p (or the equivalent quantity C_p) appearing in the equation above. These are, in fact, difficult to be evaluated *a priori* and, therefore, are estimated by fitting appropriate experimental data as part of the calibration procedure discussed later. As a consequence, they empirically account for all the other model errors, arising particularly in the density evaluation through eqs. (13) and (14).

Table I Recipes of the Homopolymerization Reactions

| | | Batch (Initial) ^a | | | | Pre-emulsion ^b | | | |
|-------------|-----|------------------------------|----|-----|-----|---------------------------|----|---------------|--|
| Run No. | М | W | E | Ι | М | W | E | Q | |
| Run 1 (Sty) | 200 | 938 | 10 | 1.1 | _ | _ | _ | _ | |
| Run 2 (VAc) | 200 | 938 | 10 | 1.1 | | | | | |
| Run 3 (MMA) | 200 | 938 | 10 | 1.1 | | | | | |
| Run 4 (BuA) | 200 | 938 | 10 | 1.1 | | | | | |
| Run 5 (MMA) | 50 | 674 | 4 | 1.1 | 150 | 263 | 6 | 3.0 | |
| Run 6 (MMA) | 50 | 674 | 4 | 1.1 | 150 | 263 | 6 | 12.5 | |
| Run 7 (MMA) | 100 | 500 | 6 | 1.1 | 600 | 300 | 24 | 2.2; 1.6 | |
| Run 8 (BuA) | 100 | 600 | 6 | 1.1 | 600 | 300 | 24 | 5.9; 1.9; 2.9 | |

^a M indicates the monomer (g); W, water, (g); E, emulsifier (g); I, initiator (g).

^b Q indicates the mass-specific flow rate (g g⁻¹).

| | Batch (Initial) ^a | | | | Pre-emulsion ^b | | | | | |
|------------------|------------------------------|-------|------|----|---------------------------|---------|---------|-----|----|---------------|
| Run No. | M_{1} | M_2 | W | Ε | Ι | M_{1} | M_{2} | W | E | Q |
| Sty–MMA (50°C): | | | | | | | | | | |
| Run 9 (70 : 30) | 70 | 30 | 938 | 10 | 1.1 | _ | | | _ | _ |
| Run 10 (30 : 70) | 30 | 70 | 938 | 10 | 1.1 | _ | _ | _ | | _ |
| Run 11 (30 : 70) | 113 | 262 | 938 | 10 | 1.1 | _ | _ | _ | — | |
| MMA–VAc (50°C): | | | | | | | | | | |
| Run 12 (80 : 20) | 160 | 40 | 938 | 10 | 1.1 | | _ | | _ | _ |
| Run 13 (50 : 50) | 100 | 100 | 938 | 10 | 1.1 | _ | _ | | | _ |
| Run 14 (20:80) | 40 | 160 | 938 | 10 | 1.1 | — | | | — | — |
| Sty-BuA (50°C): | | | | | | | | | | |
| Run 15 (74 : 26) | 74 | 26 | 1000 | 10 | 1.1 | | | | _ | |
| Run 16 (69 : 31) | 235 | 106 | 793 | 10 | 1.1 | | | | | |
| Run 17 (50 : 50) | 100 | 100 | 938 | 10 | 1.1 | | | | — | — |
| Sty-BuA (70°C): | | | | | | | | | | |
| Run 18 (68 : 32) | 102 | 48 | 517 | 8 | 0.8 | 243 | 113 | 99 | 21 | 1.8 |
| Run 19 (50 : 50) | 37 | 37 | 624 | 5 | 0.6 | 299 | 299 | 171 | 23 | 2.3; 1.8; 4.4 |
| Run 20 (30 : 70) | 22 | 52 | 623 | 5 | 0.6 | 178 | 415 | 169 | 23 | 1.6 |

Table II Recipes of the Copolymerization Reactions

^a M_i indicates the monomer *i* (g); *W*, water (g); *E*, emulsifier (g); *I*, initiator (g).

^b Q indicates the mass specific flow rate (g g⁻¹).

The parameter T accounts for the possible occurrence of glass transition. This typically occurs at high conversion values, which, in the case of an isothermal reactor, corresponds to the point where the glass transition temperature of the polymer-monomer mixture in the particles becomes larger than the reactor temperature. Thus, the following empirical expression has been used to represent T as a function of the monomer volume fraction in the particle, as follows:

$$T=1 \hspace{1cm} ext{if} \hspace{1cm} \phi_m \geq \phi_{cr}$$

(low-intermediate conversion) (16)

$$T = \left(rac{1-\phi_{cr}}{1-\phi_m}
ight)^b \hspace{0.4cm} ext{if} \hspace{0.4cm} \phi_m < \phi_{cr}$$

(high conversion) (17)

where ϕ_{cr} and *b* are adjustable parameters, to be evaluated by fitting, and $\phi_m = \Sigma \ \phi_{mi}$. The expression for *T* given by eq. (17) has been selected based on the experimental trend. In particular, it was required that T = 1 at $\phi_m = \phi_{cr}$ for continuity with eq. (16) and that *T* decreases as the monomer content decreases. The compressibility of the swollen particle has, in fact, to approach the compressibility of the pure polymer as ϕ_m approaches 0. While the value of b controls the nonlinearity of this decreasing behavior, the parameter ϕ_{cr} could be regarded as the volume fraction of the monomer mixture at which glass transition occurs. Its evaluation can be performed independently taking advantage of the ultrasound attenuation behavior in batch reactions, as shown in Figure 2, in the case of homopolymerization. By inspection of the data reported in the figure, it is easily verified that the following three different cases are possible: the curve exhibits a single maximum value at high conversion (Sty and MMA); two maxima are evidenced, one at low and the other at high conversion (VAc); and no maxima at all are found (BuA). While the maximum value at low conversion could be ascribed to different phenomena external to the particle (e.g., nucleation, polymerization in aqueous phase, etc.), the one at high conversion is somehow related to a change of the polymer state, as in the case of the glass transition. Since this involves also a change in the polymer particle compress-

| Measurement | MMA | Sty | VAc | BuA | Reference Source |
|--|-----------------|-----------------|-----------------|------------------|---------------------|
| Reactivity ratios | | | | | |
| r _{MMA,i} | 1.00 | 0.46 | 26.00 | 2.86 | 20 |
| r _{Sty i} | 0.52 | 1.00 | 57.80 | 0.70 | 20 |
| $r_{\rm VAci}$ | 0.03 | 0.08 | 1.00 | 0.02 | 20 |
| r _{BuA} i | 0.12 | 0.20 | 3.48 | 1.00 | 20 |
| Water solubility (g g_w^{-1}) | $1.58 10^{-2}$ | $6.70 10^{-5}$ | $2.84 10^{-2}$ | $7.86 \ 10^{-3}$ | 21,22 |
| Maximum swelling (monomer saturation in particle) (ϕ_{*}^{*}) | 0.77 | 0.73 | 0.84 | 0.69 | 19,23,21,24 |
| Monomer density $(g \text{ cm}^{-3})$ | 0.908 | 0.878 | 0.895 | 0.865 | 20,25 |
| Homopolymer density (g cm $^{-3}$) | 1.16 | 1.11 | 1.17 | 1.08 | 20,26 |
| Homopolymer glass transition temperature T_{σ} (°C) | 105 | 100 | 30 | -54 | 20,26 |
| Monomer sound velocity (m s^{-1}) | 1064 | 1273 | 1003 | 1089 | 9 |
| Polymer sound velocity (m s ⁻¹) (C_{r}^{f}) | 1940 | 1850 | 1515 | 1250 | 9 |
| Polymer sound velocity (literature range of values) | 1340–2690 | 1150-2400 | 730–1830 | 810–2000 | 27,26 |
| Water density (g cm $^{-3}$) | | | | 0.9895 | 3 |
| Water sound velocity (m s^{-1}) | | | | 1543 | 3 |

Table III Values of Model Parameters Obtained from Independent Sources at $T = 50^{\circ}$ C

ibility, the value of ϕ_{cr} has been assumed equal to that of the monomer volume fraction in the particles corresponding to the onset of the attenuation increase.

The parameter $\Delta\beta_{par}$ is introduced to account for the nonideal behavior of the particle compressibility before the glass transition. In order to account for the dependence of this quantity on the monomer volume fraction in the particle, the following empirical expression derived in the Appendix has been used:

$$\Delta \beta_{\text{par}} = \phi_m (1 - \phi_m) (\beta_p - \beta_m)$$
$$\times [1 - 2\phi_m + \phi_m (1 - \phi_m) (1 - G)] \quad (18)$$

where the compressibility of the monomer mixture is calculated as a volume average of the same quantities corresponding to pure monomers ($\beta_m = \Sigma \ \beta_{mi} \phi_{mi} / \phi_m$), and *G* is defined as

$$G = \frac{\phi_{mG}^3 - 2\phi_{mG} + 1}{\phi_{mG}^3 - 2\phi_{mG}^2 + \phi_{mG}}$$
(19)

In this case, ϕ_{mG} is the adjustable parameter, specific for each particular system, to be evaluated during the calibration procedure.

Finally, an additional comment on β_p is required. Its value refers to the polymer before the glass transition, that is, at T = 1. Therefore, apart from the particular case of a polymer produced at a reaction temperature above its T_g , its value is different from that of the polymer in the final, glassy state. To better evidence this difference, the final compressibility has been indicated as β_p^f and corresponds to the value usually found

Table IV Modified Values of Model Parameters at $T = 70^{\circ}C^{a}$

| Value | Sty | BuA | Source |
|---|--------|-------|--------|
| Monomer density (g cm ⁻³) | 0.860 | 0.855 | 28 |
| Homopolymer density $(g \text{ cm}^{-3})$ | 1.043 | 0.991 | 28 |
| Monomer sound velocity (m s^{-1}) | 1192 | 1013 | 9 |
| Water density (g cm ⁻³) | 0.9835 | | 28 |
| Water sound velocity $(m \ s^{-1})$ | 1551 | | 9 |

^a Remaining values as in Table III.

| Value | ϕ_{mG} | ϕ_{cr} | b | $\begin{array}{c} C_p \\ ({\rm m~s^{-1}}) \end{array}$ |
|--|--------------------------------|----------------------|----------------------|--|
| MMA (run 3) Sty (run 1) VAc (run 2) BuA (run 4) | $0.57 \\ 0.26 \\ 0.80 \\ 0.45$ | 0.40 0.38 0.25 | 0.58 0.77 1.13 | $1750 \\ 1600 \\ 1300 \\ 1250$ |

in the literature when looking for the physical properties of a polymer.

Thus summarizing, two among the original adjustable parameters in eq. (15), T and $\Delta\beta_{par}$, have been recast in terms of ϕ_{cr} , b, and ϕ_{mG} . The overall number of parameters to be determined by fitting is therefore four, that is, the last three plus β_p .

Composition-Conversion Model

In order to use the model presented above for sound propagation velocity, we need to couple it with an additional set of equations that compute the volume hold-up of the dispersed phases (Φ_d and Φ_{par}) together with their compositions (ϕ_{mi} and $\hat{\phi}_{di}$) and the composition of the produced copolymer (ϕ_{ni}) . A model that describes the evolution of all these quantities as a function of conversion, referred to as the composition-conversion model, has been developed elsewhere.¹⁵ Accordingly, we do not discuss it here in detail. It is sufficient to mention that the model constitutive equations are material balances of monomers and copolymer as well as monomer interphase partitioning laws. The involved parameters are reactivity ratios and monomer solubilities in aqueous and polymer phases. These values are usually available in the literature for a large set of copolymer systems produced in emulsion, such as for example those considered in this work. It has been shown that this model does not require parameter fitting and produces rather accurate predictions.¹⁵ Thus, by coupling this set of equations to eq. (10) and to the auxiliary expressions leas. (11) to (19)], we can evaluate for any given conversion value all the parameters mentioned above, that is, ϕ_{mi} , ϕ_{pi} , ϕ_{di} , Φ_d , and Φ_{par} , as well as the velocity of sound propagation C_e .

The Calibration Procedure

The online estimation of conversion in a reacting system through ultrasound velocity measure-

ments is performed using the model presented above after a suitable calibration. The calibration procedure is intended to estimate the adjustable model parameters mentioned above, that is, β_p , ϕ_{mG} , ϕ_{cr} , and b. It is assumed that reliable values of the following quantities are available: initial amounts of monomers and water, feed flow rates of monomers and water, monomer solubilities in water and particle, reactivity ratios, densities of monomers, homopolymers and water, and sound velocities (or compressibilities) of monomers and water. Moreover, the calibration procedure can be performed in the same unit used for monitoring the polymerization reaction. It is based on the following steps.

- 1. A batch reaction is performed and both sound velocity and attenuation data are collected online as a function of time;
- 2. the corresponding conversion values are obtained through an independent offline technique, such as gravimetric analysis;
- 3. for each pair of measured conversion and sound velocity values and using the composition-conversion model, eq. (10) can be solved with respect to β_{par} to produce an experimental plot of the particle compressibility as a function of ϕ_m ;
- 4. by inspection of the attenuation data, ϕ_{cr} is estimated as the monomer volume fraction in particle at the onset of the peak in sound attenuation at high conversion (if no peak is detected, this value is simply put to 0);
- 5. the parameters ϕ_{mG} and β_p are estimated by fitting eq. (15), with T = 1, to the experimental data in the range of monomer volume fraction between ϕ_m^* and ϕ_{cr} , that is, between the maximum swelling and the monomer concentration corresponding to the glass transition;
- 6. the parameter b is obtained by fitting eq.

Table VIValues of Model ParametersEstimated by Fitting: Sty-MMACopolymerization Reactions

| Sty-MMA | ϕ_{mG} | ϕ_{cr} | b | $\begin{array}{c} C_p \\ ({\rm m~s}^{-1}) \end{array}$ |
|---|--------------------------------|--------------------------------|--------------------------------|--|
| 0 : 100 (run 3) 30 : 70 (run 10) 70 : 30 (run 9) 100 : 0 (run 1) | $0.57 \\ 0.48 \\ 0.40 \\ 0.26$ | $0.40 \\ 0.40 \\ 0.40 \\ 0.38$ | $0.58 \\ 0.47 \\ 0.66 \\ 0.77$ | $1750 \\ 1750 \\ 1580 \\ 1600$ |



(15), with T now given by eq. (17), to the experimental data for $\phi_m < \phi_{cr}$.

The above calibration procedure has been applied to several systems, including both homo- and copolymers. In the second case, the adjustable quantities ϕ_{cr} , ϕ_{mG} , and β_p have been evaluated for each particular copolymer composition. The estimated values of all the adjustable parameters and the resulting performances of the calibrated conversion sensor are discussed in the next section for various polymerization systems.

EXPERIMENTAL DATA AND COMPARISONS WITH THE MODEL

In order to test the reliability of the ultrasonic sensor in estimating online conversion and composition, several homo- and copolymerization reactions were performed. Both batch and semibatch reactions have been considered at different polymer contents in order to account for the most common industrial applications. The reaction recipes are summarized in Tables I and II. Most of the experiments have been performed at 50°C. Occasionally, a higher temperature value (70°C) has been considered. The numerical values of all model parameters, available a priori or estimated by fitting, are summarized in Tables III-VI, together with the corresponding sources. Two minor specifications are as follows: (1) the reported values of the homopolymer sound velocity correspond to the final, glassy polymer (C_p^f) . As already discussed in the section on sound velocity in emulsion polymerization systems, they are expected to be different (and, in particular, larger) than the C_{ν} values involved in eq. (15); (2) when dealing with copolymers, the monomer volume fraction at saturation, ϕ_m^* , has been estimated as a simple arithmetic average between the values of the corresponding homopolymers.

Homopolymerization Batch Reactions

Polystyrene

The calculated particle compressibility as a function of monomer volume fraction is compared to the experimental data in Figure 3(a) (run 1 in Table I). Three curves are shown. The dashed straight line corresponds to the ideal case; that is, $\beta_{\rm par}$ is calculated through eq. (15) with $\Delta\beta_{\rm par} = 0$ and T = 1. The dash-dotted line curve accounts for mixture nonidealities while neglecting the polymer glass transition [that is, eq. (15) with T = 1]. The value of ϕ_{mG} is given by the ϕ_m value where these two curves intersect. Finally, the continuous curve is calculated using the complete version of eq. (15) accounting for the polymer transition taking place at $\phi_m = \phi_{cr}$. Note that at smaller conversion values (i.e., at larger ϕ_m values), dotted and continuous curves are superimposed since T = 1. On the other hand, at larger conversion values, the essential role of T is apparent. The final description of the particle compressibility is reasonably accurate, and this is reflected by the satisfactory prediction of the evolution of sound velocity with conversion, which is compared with the values measured offline by gravimetry in Figure 3(b). Three different regimes can be identified in the figure. At low conversion, a weak sensitivity of the sound velocity to conversion is apparent. This corresponds to the so-called intervals I and II of the reaction before the disappearance of the monomer droplets. Then, a significant increase of sound velocity is observed at intermediate conversion values. Finally, at a conversion value corresponding to ϕ_{cr} , the sensitivity of the sound velocity to conversion suddenly increases as a consequence of polymer glass transition. In the same figure the dashdotted line curve obtained using the model with T= 1 is also shown to evidence the role of the correction term T. It is clear that after the monomer droplets disappearance, the increase of the sound velocity is the result of the increase of a component with low compressibility, the polymer, at the expenses of one with larger compressibility, the monomer.

Polyvinyl Acetate

Particle compressibility versus monomer volume fraction and sound velocity versus conversion are shown in Figure 4(a) and (b), respectively (run 2 in Table I), with all symbols having the same

Figure 3 (a) Particle compressibility versus monomer volume fraction and (b) sound velocity versus conversion. Sty homopolymerization, experimental data: (\Box) run 1. Calculated curves: (—) eq. (15); (---) eq. (15) with $\Delta\beta_{par} = 0$ and T = 1; (-.-) eq. (15) with T = 1. The vertical dashed lines indicate droplet disappearance (ϕ_m^*) and the values of ϕ_{mG} and ϕ_{cr} .



meaning as in the previous case. Again, the agreement between calculated and experimental data is generally satisfactory. Inaccuracies in the sound velocity prediction are evidenced at low conversion before the monomer droplets disappearance. A possible reason is that the effect of the monomer solubilized in the aqueous phase on the sound velocity in this phase is neglected in the model. This may lead to larger errors in the case of monomers exhibiting larger water solubilities, such as vinyl acetate. Note the different behavior of the particle compressibility in the case of polystyrene and polyvinyl acetate: while ϕ_{cr} is larger than ϕ_{mG} in the first case, the opposite is true in the second case.

Polymethyl Methacrylate

Particle compressibility versus monomer volume fraction and sound velocity versus conversion are shown in Figure 5(a) and (b). In these figures, data relative to both batch and semibatch reactions are shown together. For the moment, let us focus on the batch data only (run 3 in Table I; symbol \diamond in the Fig. 5). It appears that the behavior of the system is similar to that of the two previous cases.

Polybutyl Acrylate

In this case (run 4; symbol \Box), the experimental data of particle compressibility shown in Figure 6(a) are well described by eq. (15) without the correction term related to polymer glass transition (i.e., T = 1). Keeping in mind that no maximum value in the attenuation versus conversion curve was evidenced for this monomer in Figure 2, this result is consistent with the low T_g value of this polymer, lower than the reaction temperature (cf. Table III). The agreement in terms of sound velocity as a function of conversion is satisfactory [Fig. 6(b)].

In conclusion, the model and its calibration procedure developed above are able to simulate the sonic behavior of all examined systems. The estimated values of the adjustable model parameters are collected in Table V. It is worth noting that they exhibit the expected qualitative trends. In particular, the values of ϕ_{cr} are ordered according to the decreasing glass transition temperatures of the polymers. In other words, the polymer glass transition is expected to take place at increasing conversion values from polyMMA to polySty, polyVAc, and polyBuA, that is, at decreasing values of the monomer volume fraction in the polymer particles. Moreover, the value of the polymer compressibility before glass transition (reported in the table in terms of the corresponding sound velocity, C_p) results is always larger than the final value after glass transition and within the literature range of values (cf. Table III).

Homopolymerization Semibatch Reactions

Semibatch operation is the typical operating mode in industrial applications because of its better performances in terms of product quality and thermal control. Usually, the reaction is performed in the following three steps: (1) an initial batch characterized by a low value of the monomer-to-water ratio and aimed at the production of a polymeric seed; (2) a semibatch stage where the so-called pre-emulsion (water, emulsifier, and monomers) and an initiator solution are fed to the reactor; (3) a final batch where the complete depletion of the residual monomer is seeked.

In this section, four semibatch reactions are discussed. The aim is to show that, after the calibration performed through a single batch reaction, the model becomes fully predictive with respect to variations of the operating mode and the monomer-to-water ratio. MMA and BuA have been selected as test monomers due to their different behavior from the sonic viewpoint (largely different glass transition temperatures, and polymer sound velocity larger and smaller than that in water phase, respectively). Note that in all cases, a constant addition flow rate specific to the amount of produced polymer (g of monomer per g of polymer) has been used (cf. recipes in Table I). It is clear that in order to implement this feed policy, we need to know online the actual conversion in the reactor, which is precisely the infor-

Figure 4 (a) Particle compressibility versus monomer volume fraction and (b) sound velocity versus conversion. VAc homopolymerization, experimental data: (\Box) run 2. Calculated curves: (—) eq. (15); (- - -) eq. (15) with $\Delta\beta_{\rm par} = 0$ and T = 1; (-.-.) eq. (15) with T = 1. The vertical dashed lines indicate droplet disappearance (ϕ_m^*) and the values of ϕ_{mG} and ϕ_{cr} .





Figure 5 (Continued from the previous page)

mation given by the sensor. Thus, the pump flow rate was continuously adjusted by the computer based on the signal received from the sonic sensor. The comparison *a posteriori* of the added amount as a function of conversion with the target value is therefore a further check of the sensor reliability.

In Figure 5(b) and (c), the sound velocity versus conversion data for three different MMA semibatch reactions are shown (run 5, 6, and 7 in Table I). Let us first examine runs 5 and 6 [symbols \Box and \triangle , respectively, in Fig. 5(b)]. With the exception of the feed rate of the monomer to the reactor, both recipes are fully equivalent to the corresponding batch case, Run 3 (symbol \diamond in the same figure). The transitions among the three operation steps described above are easily identified by the slope discontinuities of the sound velocity curves. After the expected sound velocity increase during the initial batch step, the two semibatch reactions exhibited an opposite behavior, with increasing velocity in Run 5 and decreasing velocity in Run 6. This difference is due to the feed flow rate. If the flow rate value is small enough, the monomer consumption by reaction is not counterbalanced by its addition, and the net result is a decreasing residual monomer, as in a batch reaction. Thus, the velocity of sound increases as in Run 3. On the other hand, for large values of the feed flow rates, the monomer accu-

Figure 5 (a) Particle compressibility versus monomer volume fraction; (b) and (c) sound velocity versus conversion. MMA homopolymerization, experimental data: (\diamond) run 3; (\Box) run 5; (\triangle) run 6; (*) run 7. Calculated curves: (—) eq. (15); (- -) eq. (15) with $\Delta\beta_{\rm par} = 0$ and T = 1; (-.-.) eq. (15) with T = 1. The vertical dashed lines indicate droplet disappearance (ϕ_m^*) and the values of ϕ_{mG} and ϕ_{cr} .







Figure 6 (Continued from the previous page)

mulates in the reactor and, being its compressibility value larger than that of water, the sound velocity in the system decreases with conversion. The evolution of the sound velocity in both reactions is well predicted by the model (continuous curves in the figure). With respect to industrial applications, it is worth noting that the sonic behavior exhibited by this monomer when operating the polymerization reaction in semibatch mode can be fully exploited to monitor the monomer accumulated in the system even in a qualitative way. In fact, if "starved" conditions are desired (rate of reaction limited by the monomer addition), the measured sound velocity should be always increasing. A monomer build up in the reactor is readily detected by the sensor and, when

desired, the corresponding feed flow rate adjustment can be immediately performed, for example, to prevent thermal runaway.

In run 7 [Fig. 5(c)], a large value of the monomer-to-water ratio has been considered together with a complex monomer feed policy (after the initial batch step, two different flow rates have been used). The result is the discontinuous behavior of the sound velocity with conversion reported in the figure. It is worth noting that the model correctly predicts this evolution, thus confirming its reliability even in the case of reaction conditions relatively far from those of the calibration run.

The results of a semibatch reaction involving BuA are shown in Figure 6(c) (run 8 in Table I).

Figure 6 (a) Particle compressibility versus monomer volume fraction; (b) and (c) sound velocity versus conversion. BuA homopolymerization, experimental data: (\Box) run 4; (\bigcirc) run 8. Calculated curves: (—) eq. (15); (- -) eq. (15) with $\Delta\beta_{par} = 0$. The vertical dashed lines indicate droplet disappearance (ϕ_m^*) and the values of ϕ_{mG} .



| Table VII | Values of Model Parameters |
|-----------|----------------------------|
| Estimated | by Fitting: MMA–VAc |
| Copolyme | rization Reactions |

| MMA–VAc | ϕ_{mG} | ϕ_{cr} | b | $C_p \ ({ m m~s^{-1}})$ |
|--|--|---|--|--|
| 100 : 0 (run 3) 80 : 20 (run 12) 50 : 50 (run 13) 20 : 80 (run 14) 0 : 100 (run 2) | $0.57 \\ 0.70 \\ 0.80 \\ 0.80 \\ 0.80 \\ 0.80$ | $\begin{array}{c} 0.40 \\ 0.41 \\ 0.39 \\ 0.29 \\ 0.25 \end{array}$ | $0.58 \\ 0.81 \\ 0.70 \\ 1.06 \\ 1.13$ | $1750 \\ 1490 \\ 1470 \\ 1390 \\ 1300$ |

Three different feed flow rates have been considered together with an additional intermediate batch step between the last two addition intervals, in addition to the usual initial and final batch stages. This leads to a rather complex behavior of the sound velocity as a function of conversion, but the model predictions remain in close agreement with the experimental results. Note that in this case, the sound velocity always decreases during the semibatch intervals, even at relatively low values of the addition flow rate. This is due to the relative value of the sound velocity in polymer and water. If ${\cal C}_p > {\cal C}_w$ (as in the case of MMA), the sound velocity increases if the monomer addition rate is lower than its reaction rate, while it decreases if the monomer addition rate is higher than reaction rate. On the other hand, if $C_p < C_w$ (as in the case of BuA), the monomer addition always results in sound velocity values decreasing with conversion.

As a further check of the developed model, the cumulative amounts of monomer charged to the reactor as a function of conversion are shown in Figure 7(a) for MMA (run 5, 6, and 7 in Table I) and Figure 7(b) for BuA (run 8 in Table I), respectively. As discussed above, the agreement between the target addition profiles (calculated lines) and the corresponding experimental data (symbols) confirms the reliability of the sensor for conversion monitoring.

Copolymerization Batch Reactions

In the case of copolymers, an additional complication arises from the so-called compositional

Table VIIIValues of Model ParametersEstimated by Fitting: Sty-BuACopolymerization Reactions

| Sty–BuA | ϕ_{mG} | ϕ_{cr} | b | $\begin{array}{c} C_p \\ ({\rm m~s}^{-1}) \end{array}$ |
|---------------------|-------------|-------------|------|--|
| $T = 50^{\circ}$ C: | | | | |
| 100 : 0 (run 1) | 0.26 | 0.38 | 0.77 | 1600 |
| 74 : 26 (run 15) | 0.36 | 0.28 | 1.07 | 1490 |
| 69 : 31 (run 16) | 0.31 | 0.23 | 1.33 | 1470 |
| 50 : 50 (run 17) | 0.38 | 0.17 | 1.03 | 1390 |
| 0:100 (run 4) | 0.45 | _ | _ | 1250 |
| $T = 70^{\circ}$ C: | | | | |
| 68 : 32 (run 18) | 0.31 | 0.10 | 1.00 | 1420 |
| 50 : 50 (run 19) | 0.38 | — | — | 1355 |
| 30:70 (run 20) | 0.45 | | _ | 1310 |

drift. This is due to the different reactivities of the two monomers (usually expressed in terms of reactivity ratios; r_{ij} values in Table III) which, when operating in a batch reactor, lead to a polymer composition which changes during the reaction. This composition change is accounted for in the developed model through the compositionconversion model mentioned in the Sound Velocity in Emulsion Polymerization Systems section. Another relevant aspect is the dependence of the parameter ϕ_{cr} , corresponding to the onset of the glass transition, upon the copolymer composition. In particular, when the two homopolymers are characterized by largely different glass transition temperatures, a significant variation of ϕ_{cr} with copolymer composition is expected.

To better analyze the performance of the calibration model in the case of copolymers, different systems have been considered. First, the copolymer Sty–MMA, characterized by negligible compositional drift and very similar T_g values for the two corresponding homopolymers has been examined. This is the best situation to check the reliability of the mixing rules for copolymers adopted in the auxiliary equations of the calibration model [eqs. (11)–(19)]. Next, two copolymers (MMA–VAc and Sty–BuA), characterized by different compositional drifts and T_g values, have been considered. The estimated values of all the adjustable quantities have been summarized in three tables

Figure 7 Cumulative pre-emulsion amount charged to the reactor versus conversion. Semi-batch homopolymerization reactions of (a) MMA and (b) BuA. Experimental data: (\Box) run 5; (\triangle) run 6; (*) run 7; (\bigcirc) run 8; (—) amount calculated (target).



(a)

Styrene–Methyl Methacrylate

Three experiments have been performed (runs 9, 10, and 11 in Table II), in order to analyze separately the role of composition and monomer-towater ratio. In Figure 8(a), the particle compressibility data are shown as a function of monomer volume fraction ϕ_m for all reactions. In the same figure are also shown the results obtained by model fitting, with the parameter values summarized in Table VI. It is apparent that the estimated value of ϕ_{cr} is independent of the monomer-to-water ratio and of composition. Both these results are reasonable on physical ground, but only the first one is of general validity. The second one is coincidental and is due to the similarity between the T_g values of the two homopolymers under consideration (cf. Table III). The onset of the polymer phase transition is, in fact, at $\phi_m =$ 0.40 for all copolymers, a value equal to that of MMA and very close to that of Sty. About the remaining adjustable parameters (ϕ_{mG} , b, and C_p in Table VI), in general, their values are intermediate between those of the corresponding homopolymers and exhibit the expected trends with the polymer composition (e.g., increasing ϕ_{mG} and C_p values for increasing MMA content). In terms of sound velocity versus conversion data [Fig. 8(b)], good agreement between experimental data and model results is found in all cases.

Methyl Methacrylate–Vinyl Acetate

In this case, due to the largely different reactivities of the two monomers (cf. r_{ij} values in Table III), a relevant compositional drift is expected. Moreover, the two homopolymers are characterized by rather different T_g values, thus indicating a strong dependence of T_g on composition for the corresponding copolymers. Three experiments at different compositions have been performed (runs 12, 13, and 14 in Table II). The obtained results are shown in Figure 9(a) and (b) in terms of particle compressibility versus monomer volume fraction and sound velocity versus conversion, respectively. It is seen that for an increasing MMA content, the occurrence of the glass transition is anticipated at lower conversion values, which is consistent with the increase of the estimated values of ϕ_{cr} shown in Table VII. About the values of the other adjustable parameters, no clear trend with copolymer composition can be evidenced. Finally, it is worth noting that the prediction of the sound velocity behavior with conversion is very poor at low conversion values, that is, in the presence of monomer droplets. Similarly to the case of VAc homopolymerization, as discussed in the context of Figure 4(b), this is due to the large water solubility of VAc, which alters the physical properties of the aqueous solution with respect to those of pure water.

Styrene–Butyl Acrylate

This system is characterized by a weak compositional drift, certainly lower than that of the previous case. Moreover, one of the polymerization reactions has been performed at azeotropic conditions (run 16), that is, in the absence of compositional drift. On the other hand, the T_g values of the two homopolymers are rather different, thus indicating a strong dependence of the copolymer T_{σ} on its composition. This implies that for each run with different copolymer composition, a different value of ϕ_{cr} has to be used in the model. The previous statement is confirmed by the comparison between measured and computed values of the particle compressibility as a function of ϕ_m shown in Figure 10(a), where the values of ϕ_{cr} are indicated by vertical lines. The numerical values of this and the other model adjustable parameters are summarized in Table VIII (reactions at T $= 50^{\circ}$ C). It can be seen that the onset of the phase transition is largely delayed (i.e., it takes place at lower ϕ_m values) for increasing BuA content, and it is indeed absent in the case of BuA homopolymerization, as discussed earlier. The model results are compared with the experimental data in terms of sound velocity versus conversion in Figure 10(b).

Figure 8 (a) Particle compressibility versus monomer volume fraction and (b) sound velocity versus conversion. Sty–MMA copolymerization, experimental data: (*) run 9; (\triangle) run 10; (\Box) run 11; (—) calculated curves. The vertical dashed lines indicate droplet disappearance (ϕ_m^*) and the value of ϕ_{cr} .





Copolymerization Semibatch Reactions

The last case considered here is probably the most interesting one with respect to industrial applications. The usual industrial procedure for producing copolymers with uniform composition is, in fact, to operate semibatch reactors with appropriate monomer feed policies. Two different approaches can be used¹⁶: policy I (or starved), where the addition rate is very slow and becomes the rate-limiting step of the reaction $process^{17}$; and policy II, where the monomer addition flow rates are evaluated a priori to maximize the reaction rate and are then implemented using a suitable online monitoring of conversion.^{18,19} Note that in the first case, a constant flow rate monomer mixture with constant composition, and equal to that of the polymer to be produced, is fed to the reactor. On the other hand, variable flow rates are used in the second one.

To test the potential of the developed conversion sensor, three semibatch reactions have been carried out using Sty and BuA. Three different compositions have been analyzed (runs 18, 19, and 20 in Table II) at a temperature value larger than that in all previous reactions ($T = 70^{\circ}$ C). In all cases, after an initial period in which the reactor was operated in the batch mode, starved operating conditions have been adopted. Thus, a constant composition monomer mixture (with the same monomer content of the desired copolymer) was fed, with a flow rate always lower than the potential polymerization rate. As a consequence, during the semibatch steps, the reaction rate was practically constant in all the experimental runs. The corresponding flow rate values have been reported in Table II in terms of the mass specific flow rate Q. Note that in runs 18 and 20, a constant flow rate has been used, while in run 19, three different values have been adopted. In all cases, the final portion of the reaction was conducted again in the batch mode.

It is worth noting that since these runs have been performed at different operating temperatures, the values of the model parameters have to be modified with respect to those reported in Table VIII for the batch reactions. Therefore, these reactions may be regarded as the calibration runs, at three different copolymer compositions, for subsequent composition-controlled copolymerizations. About the values of the model parameters obtained from independent literature sources (Table III), only densities of monomer, polymer, and water, as well as monomer and water sound velocities, have been corrected for the temperature change, and the corresponding numerical values are summarized in Table IV. All the remaining parameters have been used as in Table III without temperature correction.

The sound velocity values are shown in Figure 11 as a function of conversion for the experimental runs 18, 19, and 20. The good agreement between model predictions and experiments has been obtained using the values of the adjustable parameters ϕ_{mG} , ϕ_{cr} , b, and C_p reported in Table VIII (T = 70 °C). When compared with the corresponding values obtained earlier at $T = 50^{\circ}$ C (and listed in the same table), we see that both ϕ_{mG} and C_p are only slightly modified. On the other hand, much stronger changes are found for ϕ_{cr} , corresponding to the onset of the polymer phase transition. In this case, it is expected that an increase of reactor temperature results in a delay of the transition, which takes place at higher conversion. In fact, the value of the monomer volume fraction corresponding to the transition is significantly reduced, from 0.23 to 0.10 in the case of azeotropic conditions (runs 16 and 18). For the other two compositions (runs 19 and 20). because of the larger BuA content in the polymer, the component with the lowest T_g value, the polymer transition disappears with respect to the corresponding runs at lower temperature, run 17.

It is worth stressing that in all reactions, a rather small compositional drift was observed, and the final copolymer composition was very close to the target value, as can be seen from the copolymer composition curves as a function of conversion shown in Figure 12, as calculated through the composition-conversion model. At the same time, we noted above that the description of the evolution of the sound velocity with conversion is quite satisfactory. Therefore, the sensor is expected to give a reliable online monitoring of conversion during

Figure 9 (a) Particle compressibility versus monomer volume fraction and (b) sound velocity versus conversion. MMA–VAc copolymerization, experimental data: (\Box) run 12; (\triangle) run 13; (*) run 14; (—) calculated curves. The vertical dashed lines indicate droplet disappearance (ϕ_m^*) and the values of ϕ_{cr} .





Figure 11 (a) Particle compressibility versus monomer volume fraction and (b) sound velocity versus conversion. Sty–BuA copolymerization, experimental data: (\Box) run 18; (\triangle) run 19; (*) run 20; (—) calculated curves.

semibatch, composition-controlled reactions, which are those of major interest in applications.

CONCLUSIONS

The potential of a commercial ultrasonic probe as an online and *in situ* sensor of conversion in emulsion polymerization reactors has been shown through an extensive experimental analysis involving homo- and copolymerization reactions operated in the batch and semibatch mode. In particular, a robust and general calibration procedure of the instrument has been developed. This is based on an empirical model of the sound wave propagation in dispersed systems combined with a single, batch calibration reaction. In the case of homopolymers, the calibration is not affected by variations of recipe (i.e., relative amounts of monomer, water, and additives) and operating mode (batch and semibatch). In the case of copolymers, the calibration should be repeated for each copolymer composition. Reliable results have been obtained also in the case of significant compositional drifts, even though the best performances of the instruments are expected when operating under controlled conditions for the polymer composition, as is the case for several processes of industrial relevance.

Figure 10 (a) Particle compressibility versus monomer volume fraction and (b) sound velocity versus conversion. Sty–BuA copolymerization, experimental data: (*) run 15; (\triangle) run 16; (\Box) run 17; (-) calculated curves. The vertical dashed lines indicate droplet disappearance (ϕ_m^*) and the values of ϕ_{cr} .



Figure 12 Calculated copolymer composition versus conversion: (1) run 18; (2) run 19; (3) run 20.

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APPENDIX

Particle compressibility as a function of monomer volume fraction has been empirically expressed as a fourth-order polynomial in ϕ_m as follows:

$$\beta_{\text{par}} = A\phi_m^4 + B\phi_m^3 + C\phi_m^2 + D\phi_m + E \quad (A.1)$$

The coefficients in eq. (A.1) are evaluated by imposing the following five requirements. These are simple consistency conditions or arise from the observation of the behavior of particle compressibility versus ϕ_m data for various monomers.

• Pure monomer mixture (no polymer):

$$\beta_{\text{par}} = \sum_{i=1}^{N_m} \beta_{mi} \phi_{mi} \quad ; \quad \frac{d\beta_{\text{par}}}{d\phi_m}|_{\phi_m=0} = 0 \quad (A.2)$$

• Pure polymer (no residual monomer):

$$eta_{\mathrm{par}} = eta_p \quad ; \quad rac{deta_{\mathrm{par}}}{d\phi_m}|_{\phi_m = 1} = 0 \qquad (\mathrm{A.3})$$

• Ideal behavior at a particular concentration value, $\phi_m = \phi_{mG}$ (i.e., $\Delta \beta_{par} = 0$ at ϕ_{mG}):

$$\beta_{\text{par}}(\phi_{mG}) = \beta_{mi}\phi_{mG} + \beta_p(1 - \phi_{mG}) \quad (A.4)$$

After some manipulations, the systems of eqs. (A.2)–(A.4) is solved to give explicit expressions for A, B, C, D, and E as functions of the adjustable parameters ϕ_{mG} and β_p , which, after substitution in eq. (A.1), results in eq. (18).

NOTATION

- b empirical parameter [cf. eq. (17)]
- C sound velocity (m s⁻¹)
- G empirical quantity [cf. eq. (19)]
- $\begin{array}{ll} \mathbf{k}_{p,ij} & \text{propagation rate constant of radical } i \text{ with} \\ & \text{monomer } j \; (\mathrm{cm}^{-3} \; \mathrm{mol}^{-1} \; \mathrm{s}^{-1}) \end{array}$
- r_{ij} reactivity ratio, $k_{p,ii}/k_{p,ij}$ T empirical parameter [cf. e
- empirical parameter [cf. eqs. (16) and (17)]
- T_g glass transition temperature (°C)

Greek Letters

- β adiabatic compressibility (1/Pa)
- $\Delta\beta$ nonideal contribution to particle compressibility [cf. eq. (15), 1/Pa]
- ϵ elastic modulus (1/Pa)
- ϕ_k kth component volumetric fraction
- Φ_k kth phase volume fraction
- ho density (g cm⁻³)

Subscripts

- aq aqueous solution
- d oil droplets
- e emulsion
- *i i*th component (monomer or polymer)
- *m* monomer
- p polymer
- par particle
- w water

Superscripts

- f final value
- * saturation value

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