Densimetry for On-Line Conversion Monitoring in Emulsion Homo- and Copolymerization

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SYNOPSIS

The use of on-line densimetry to monitor conversion in batch emulsion polymerization reactors are investigated. Some characteristics of the sampling circuit connecting the reactor to the densitometer, which allow one to obtain reliable on-line estimations of monomer conversion in the whole range of conversion, are discussed in detail. Moreover, the amount of collected data provides a practically continuous monitoring of the system evolution in time, which allows one to estimate directly the rate of conversion as a function of time. The technique has been applied both to homopolymerization systems [i.e., styrene (STY) and methyl methacrylate (MMA)] as well as to copolymerization systems [i.e., STY-MMA, acrylonitrile (ACN)-MMA, vinyl acetate (VAC)-MMA]. In the latter case, the density measurements are combined with a reliable model which provides for polymer composition as a function of conversion, in order to obtain accurate measurements of monomers conversion. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many of the problems encountered in emulsion polymerization reactor control are due to the difficulty of estimating on-line the reaction evolution. In an industrial environment this usually requires measuring the reaction conversion, which can be done by monitoring either (i) the residual monomer content or (ii) the polymer content in the reactor. Both these measurements are complicated by the dispersed nature of the organic phases and the heterogeneity of the system.

In the first case (i), the residual monomer concentration can be measured through gas chromatography of the latex. Since a quantitative analysis is needed either an internal standard technique (i.e., an inert component whose amount remains constant during the reaction is introduced into the reactor) or a proper automatic sampling device[1-3] have to be used. However, a significant delay usually arises between the sampling and the analysis response. Even though this delay can be reduced by properly tuning the operating conditions of the chromatographic analysis, in general, the obtained measurements cannot be considered on-line with respect to the evolution of the reaction.

In the second case (ii), a promising approach to the estimation of polymer concentration is based on latex density measurements through an accurate capillar densitometer.[4-12] Schork[4,5] and Schork and Ray[6] used this kind of apparatus to measure monomer conversion in batch and continuous emulsion polymerization of methyl methacrylate (MMA). Some difficulties in the sampling process were encountered by Abbey,[7] who also used a densitometer for measuring conversion in batch and semibatch emulsion and solution homopolymerizations of various monomers and in batch emulsion copolymerization of butyl acrylate and MMA. Ponnuswamy et al.[8,9] used densimetry to monitor conversion in batch solution polymerization of MMA, and reported problems about pump failure at high conversion and temperature control. Moritz[10] applied densimetry to monitor conversion in the emulsion polymerization

of vinyl acetate (VAC). Caris et al.[11] determined the kinetics of emulsion polymerization of MMA in presence of modified TiO_2 using a densitometer.

In this work, the utilization of a densitometer to monitor conversion has been further studied in order to investigate its applicability to lower conversion values, i.e., including the interval I of the reaction, as well as to systems involving more than one monomer species. The technique has been applied to the following emulsion polymerization systems in a batch reactor: homopolymerization of styrene (STY) and MMA and copolymerization of STY–MMA, acrylonitrile (ACN)–MMA and VAC–MMA. In the case of copolymerization, since the polymer density depends upon its composition, there is no one-to-one relationship between latex density and polymer conversion as in the case of homopolymerization. This problem has been overcome by combining the density measurements with a simple but reliable "on-line" model for predicting polymer composition as a function of conversion.

It is remarkable that, since in all cases a relevant amount of data (more than 40/min) is obtained, the resulting on-line monitoring of conversion can be regarded, with respect to the characteristic time of the reaction, as a practically continuous signal in time.

EXPERIMENTAL

A digital densitometer manufactured by Anton Paar (DMA40 model) has been used. The density values are obtained from measurements of the natural period of oscillation (T) of a U-shaped tube filled with the sample, using the following relationship:

$$\rho = A(T^2 - B) \tag{1}$$

where A and B are temperature-dependent instrument constants which can be evaluated through calibration with reference to standard fluids (e.g., air and water). The period of oscillation is measured 43.2 times per minute. The instrument has been equipped with an ultrathermostat (accuracy $\pm 0.01°C$) for the temperature control of the measuring cell.

The sampling circuit, whose geometrical characteristics are summarized in Table I, is sketched in Figure 1. The peristaltic pump (8 rolls) has been equipped with tubing of two different materials: fluorinated elastomer (1.65 and 2 mm ID) and silicone (2 mm ID). A good mechanical behavior of silicone

Table I   Characteristic Dimensions of the Sampling Circuit

ID PTFE tubes	0.2 cm
Total volume	7 cm^3
Phase separator volume	1.2 cm^3
U-tube volume	0.7 cm^3

tubing (no failure was reported in any of the performed batch reactions) has been observed with STY; in the case of MMA, the fluorinated material has to be preferred in order to avoid swelling of the tube walls. Moreover, it has been observed that no significant difference in the obtained measurements arises when using expensive, high ID precision (1.65 mm ID), or cheap, low ID precision (2 mm ID), tubing.

The polymerization reactions have been carried out in the highly automatized batch reactor Arrhenius I (developed by Istituto Guido Donegani, ENICHEM Group), schematically shown in Figure 1.

Commercial monomers (RPE grade) have been vacuum-distilled to remove inhibitor just before reaction. Water has been deionized and distilled while the emulsifier (sodium lauryl sulfate) and the initiator (potassium persulfate) have been used without further purification. All reactants have been provided by Carlo Erba Analyticals.

ON-LINE MEASUREMENT AND SAMPLING

Difficulties concerning the application of this technique to emulsion polymerization systems have been reported in the literature[4-8]: monomer phase separation in the densitometer cell, pump failure from either monomer attack or polymer scale, measurement delay when operating in static mode (without flowing the sample). Apart from obvious considerations (minimization of the sampling circuit volume, compatibility between emulsion and circuit materials), reliable on-line estimation of conversion from density measurements of flowing streams requires some special care in installing and operating the densitometer. In the following, a summary of the most significant requirements to be fulfilled is reported.

Thermal Stability of the Sample Stream

Conversion evaluation by density measurements of flowing streams is strongly influenced by the thermal
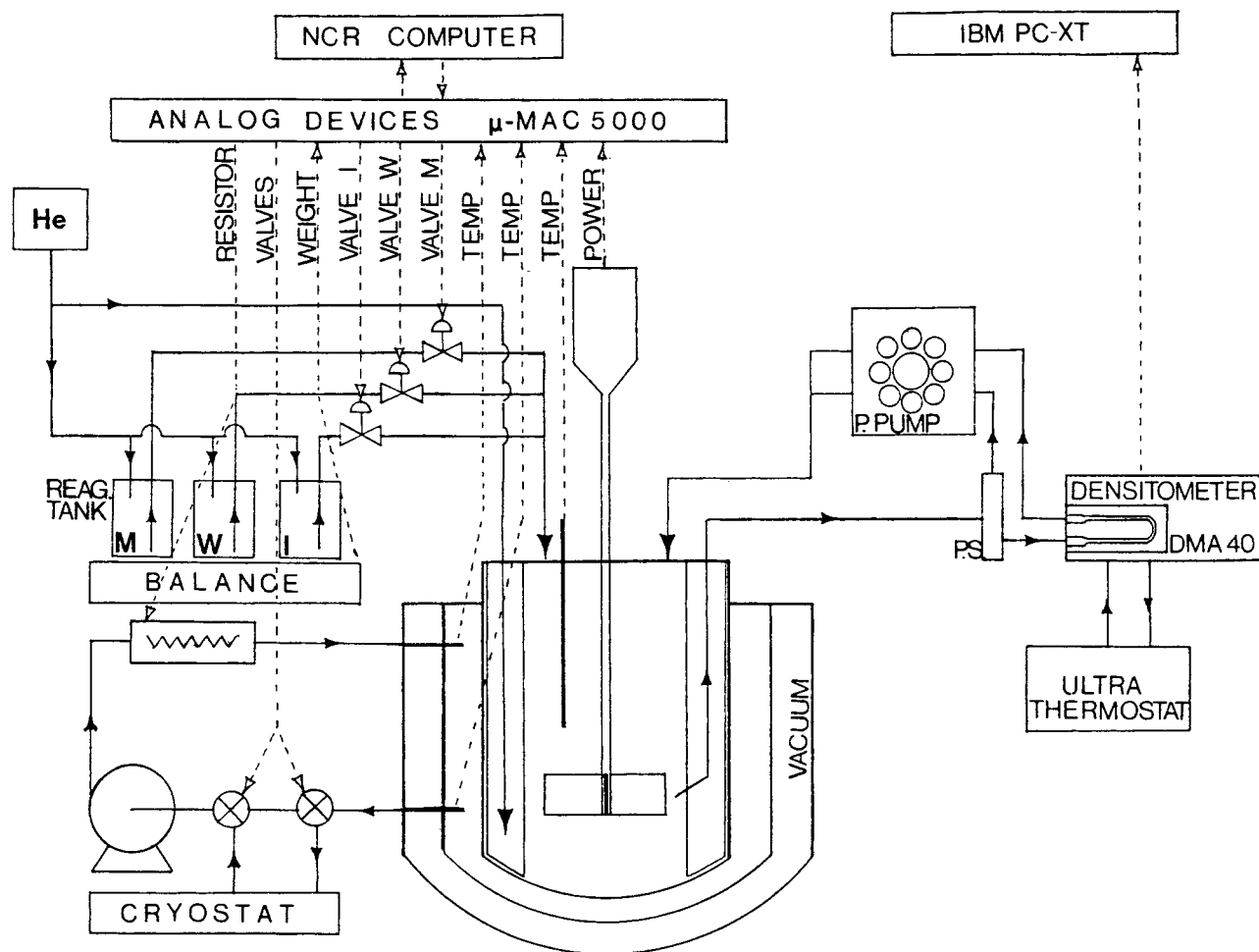
Figure 1 Scheme of the experimental apparatus.

stability of the sample. The standard thermostatting device, which comes with the instrument, is suitable for static measurements, but it may be inadequate for measurements on flowing streams. Fluctuations of the sample temperature have been observed to produce fictitious oscillations in the evaluated conversion values. This difficulty can be overcome by simply thermostatting the sample stream before entering the measurement cell through an additional heat exchanger.[5,7-9]

In this work, the temperatures of the isothermal batch reactor and of the instrument cell have been set at the same value (50°C) and the sampling circuit has been thermally insulated. The sample temperature leaving the U-shaped tube in the densitometer has been measured through a thermocouple, and a typical time evolution of the temperature value during a reaction batch is shown in Figure 2. It appears that: (i) The average temperature of the stream (about 43.6°C) is significantly different from
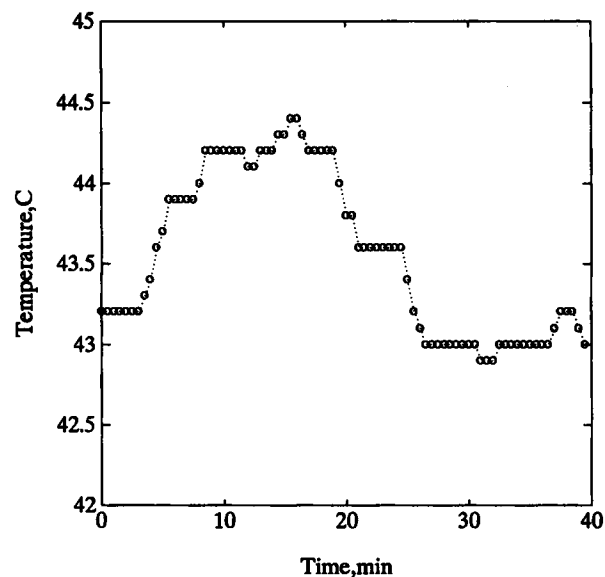

Figure 2 Sample temperature vs. time at the measurement cell outlet (run 26 of Table II).

the set point temperature of the cell (50°C), thus indicating that the instrument thermostatting device is not sufficient; (ii) the temperature fluctuations around this average value are limited to less than 1°C. The discrepancy between the actual and the set point temperatures causes some inaccuracy in conversion calculations, where, for example, the adopted density values are estimated at the set point temperature (50°C). This and similar reproducible inaccuracies have been found to affect the estimated conversion values to a negligible extent, because of the relative calibration procedure which has been adopted in this work and is described in the appropriate section. On the other hand, it can be estimated that the recorded temperature fluctuations (< 1°C) produce fluctuations of the measured density values of about 3×10^{-4} g/cm^3 leading to an error in the conversion values which does not exceed 1.5%, which is quite reasonable in the context of reactor control, even though it is larger than that typically found operating in static conditions. Thus, in conclusion, the obtained thermal stability of the sample is suf-

ficient and an additional heat exchanger has not been introduced, avoiding the corresponding increase of both sample volume and complexity of the sampling circuit.

Gas Bubbles in the Sample Stream

Bubbles in the sample cause scattering of density data. If a bubble whose diameter is comparable to that of the U-tube ($\simeq 1$ mm) flows through the measurement cell, the period value fluctuates and, eventually, falls to zero. In this case, the recorded T values and the corresponding conversion estimates are extremely scattered, as in the case shown in Figure 3, where the measured conversion values are reported as a function of time for a batch STY homopolymerization. Bubbles of various sizes are always present in the sample stream, mainly when large amounts of free emulsifier are present, i.e., during interval I of the reaction. Moreover, fluctuations in temperature and/or pressure facilitate their for-
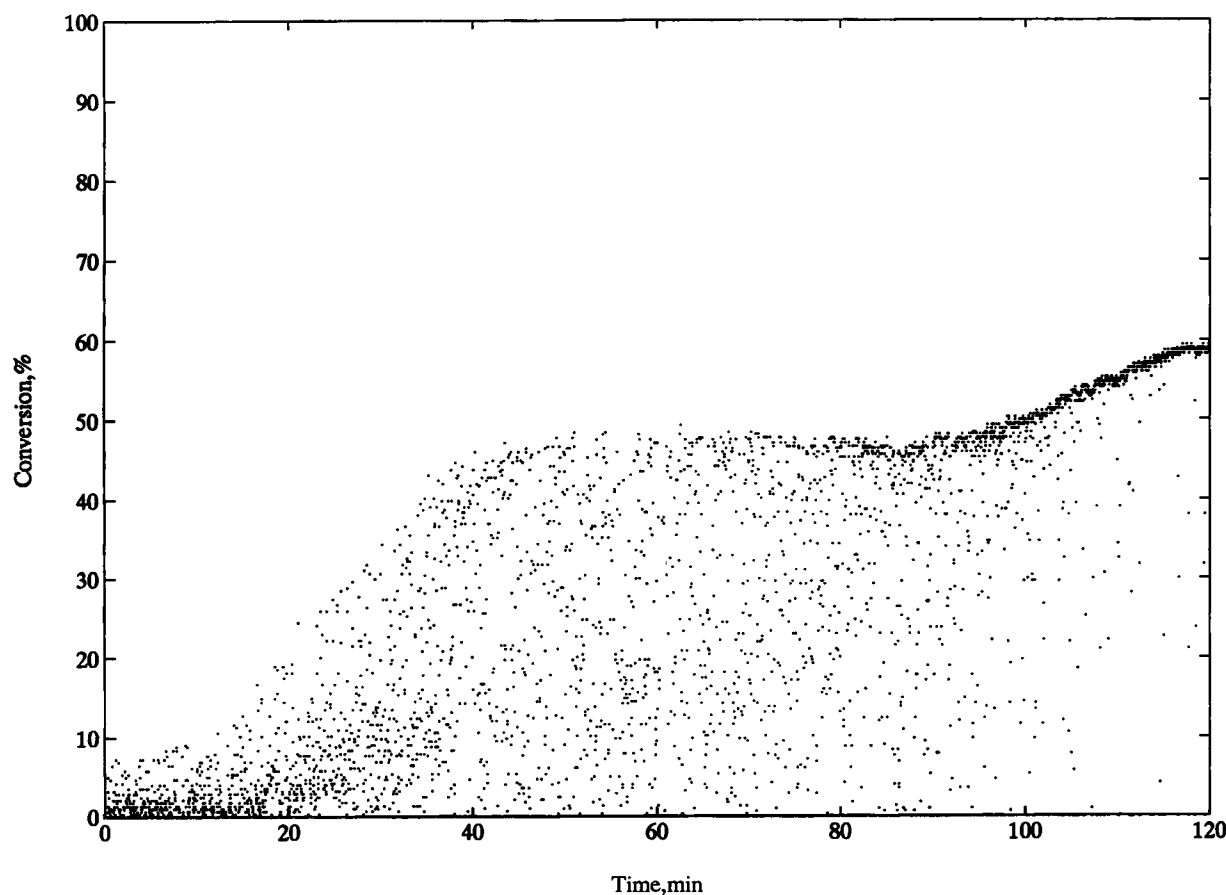

Figure 3 Conversion vs. time (run 3 of Table II); effect of gas bubbles and monomer droplets.

mation and growth, thus enhancing the disturbance on the conversion measurements.

The gas bubbles originate from the inert gas used to strip the oxygen from the emulsion before starting the reaction and to prevent air intrusion during the reaction. Both helium and nitrogen have been used, so as to test inert gases with different water solubilities, but significant differences between the two cases have not been evidenced.

A significant improvement was obtained by introducing in the sampling circuit, just before the densitometer, the phase separator sketched in Figure 4(a). In Figure 4(b), the T values referring to the same emulsion measured with and without the phase separator are shown. It appears that indeed the obtained reduction in the scattering of the measured T values is rather significant. It is worth mentioning that the residence time of the sample in the separator must be sufficient to perform complete removal of gas bubbles. This is a delicate point, since an exceedingly high residence time may have detrimental effects on the coalescence of monomer droplets. This issue is discussed in detail in the next section.

Coalescence of Monomer Droplets

The residual scattering of the measured data shown in Figure 4(b), which remains after the introduction of the phase separator, is mostly due to monomer droplets. As in the case of gas bubbles, their size is comparable to that of the U-tube. According to Abbey,[7] the relevance of this phenomenon depends upon the monomer type, and indeed we found more difficulties with STY than with MMA.

Moreover, droplets are not detected at the reactor outlet and, therefore, one can speculate that they probably grow through coalescence within the sampling circuit, where the turbulence is much lower than in the stirred reactor (600 rpm). This effect is actually even stronger since the sampling point in the reactor is located where the droplet size is minimum, i.e., near the stirrer blades, where maximum turbulence is expected.[12]

By careful inspection of the sampling circuit, it has been observed that most of the coalescence takes place in the dead volumes at the two ends of the U-tube. Such volumes have been eliminated by lengthening the PTFE tubes within the portions with enlarged section of the measuring U-tube, so as to avoid any diameter variation along the sampling circuit. This simple modification of the tubing in the instrument has been able to reduce droplet coalescence to an acceptable extent, at least after suitable selection of the sampling flow rate.

The selection of the sampling flow rate is an important factor to obtain reliable conversion measurements. The disturbance caused by a droplet that flows through the capillar depends on the velocity of the droplet itself. This is shown in Figure 5, where the recorded T values for different sampling flow rates Q are reported in the case of STY. Starting from the lower value of the droplet velocity (i.e., sampling flow rate $Q = 2.8$ g/min), it appears that the droplet influence decreases by increasing the flow rate as indicated by the decreasing scattering of the data. However, at higher flow rates, the data scattering starts to increase again, and it is accompanied by a decreases of the average value of the T data. This is the effect of the gas bubbles, which, due to the reduced retention time in the phase separator, are no longer completely removed. In conclusion, in the case of STY and with reference to the adopted sampling circuit, the best compromise between monomer droplet segregation and gas bubble removal is obtained by selecting intermediate values of the fluid flow rates, i.e., $11 \leq Q \leq 17$ g/min (see Fig. 5). A similar preliminary analysis should always be performed for any particular system so as to carefully determine the corresponding range of admissible flow rate values.

Cleaning of the Densitometer and of the Sampling Circuit

At high conversion values ($X \geq 0.8$), problems of fouling of the sampling circuit and, in particular, of the U-tube and the pump have been found, even in the case of low polymer content ($P/W \leq 0.2$). The consequence of polymer scale is a decrease of the measure reliability. Care must be used in cleaning the instrument with an appropriate cleaning cycle of solvents (e.g., emulsified water–pure water–acetone–toluene–acetone–pure water) after each reaction batch. Similarly, when a peristaltic pump is used, its tubes (which, as mentioned above, are standard and cheap silicone or fluorinated tubes, 2 mm ID) have been changed before each reaction batch so as to prevent any mechanical problem.

Relative Calibration of the Instrument

The instrument calibration constants A and B, defined by eq. (1), can be evaluated through an absolute calibration procedure, where standard fluids whose density is known precisely, and conditions as similar as possible to those adopted during the measurements are used. If the densitometer is operated in the static mode, this reduces to perform calibra-
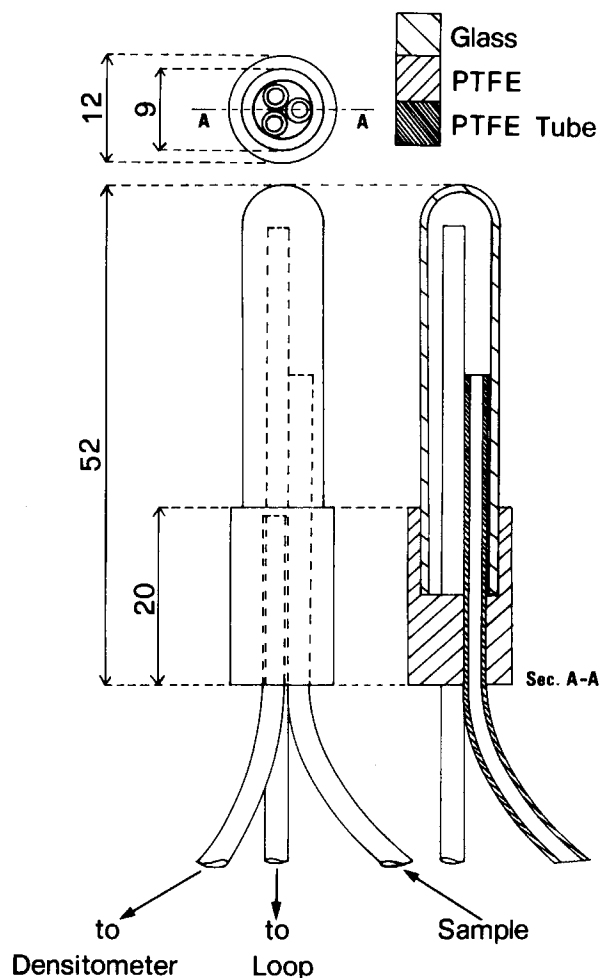
Figure 4 (a) Scheme of the phase separator (mm); (b) recorded T values without (A) and with (B) phase separator.

tion and measurements at the same temperature, which is readily achieved by allowing sufficient time for thermostatting the sample inside the measuring cell.

When the densitometer is operated under flowing conditions, a significant influence of the fluid flow rate within the sampling tube on the period of oscillation T has been observed even in the case of homogeneous samples. In particular, when increasing the fluid velocity, the mean value of T exhibits a slight drift due to the variation of the sample temperature produced by the reduced value of the sample residence time, which is not sufficient to obtain thermal equilibrium between the sample and the thermostatting fluid. Moreover, in the case of emulsion polymerization, further complications arise due to the heterogeneous nature of the sample, which can be overcome through the most suitable flow rate

selection procedure illustrated above. Thus, under flowing conditions, the absolute calibration procedure requires identical values of both the temperature and the fluid flow rate, whose value, however, may be different among various measurements because of various reasons (monomer type, bubble selection, droplet coalescence, and so on).

In order to avoid the difficulties mentioned above, the following relative calibration procedure has been adopted. A preliminary reaction batch is run, and the corresponding values of T, the period of oscillation, are recorded as a function of time. The relative calibration is then performed using as standard fluids the mixtures corresponding to the initial and final conditions of the reacting system, whose conversion values are known a priori and through gravimetry, respectively. In the homopolymer case, such a calibration procedure, performed once for each monomer, is adequate for good reproducibility. In the copolymer case, this same relative calibration requires the knowledge of both conversion and composition corresponding to each calibration point. Accordingly, the final composition of the produced copolymer (or the residual amount of each monomer) is evaluated, either experimentally or theoretically, as described in the next section.

CONVERSION EVALUATION

The reaction conversion in a batch reactor can be readily estimated from the corresponding density value (ρ) of the emulsion through the volume additivity rule. In the case of homopolymerization, the following relationship between conversion and overall density of the emulsion applies[4-6]:

$$\rho = (w + e + i + 1)$$
$$\times \left[\frac{w}{\rho_W} + \frac{e}{\rho_E} + \frac{i}{\rho_I} + \frac{1}{\rho_M} - X\left(\frac{1}{\rho_M} - \frac{1}{\rho_P}\right) \right]^{-1} \quad (2)$$

where lower case letters indicate the amount of each component referred to the initial amount of monomer (e.g., $w = W/M^0$) and ρ_j is the density of the jth component.

In the case of copolymerization, the actual compositions of both the reacting monomer mixture and the produced polymer have to be known for estimating conversion from an emulsion density value. In particular, eq. (2) can be used again, where ρ_M and ρ_P are redefined as the average density of mono-
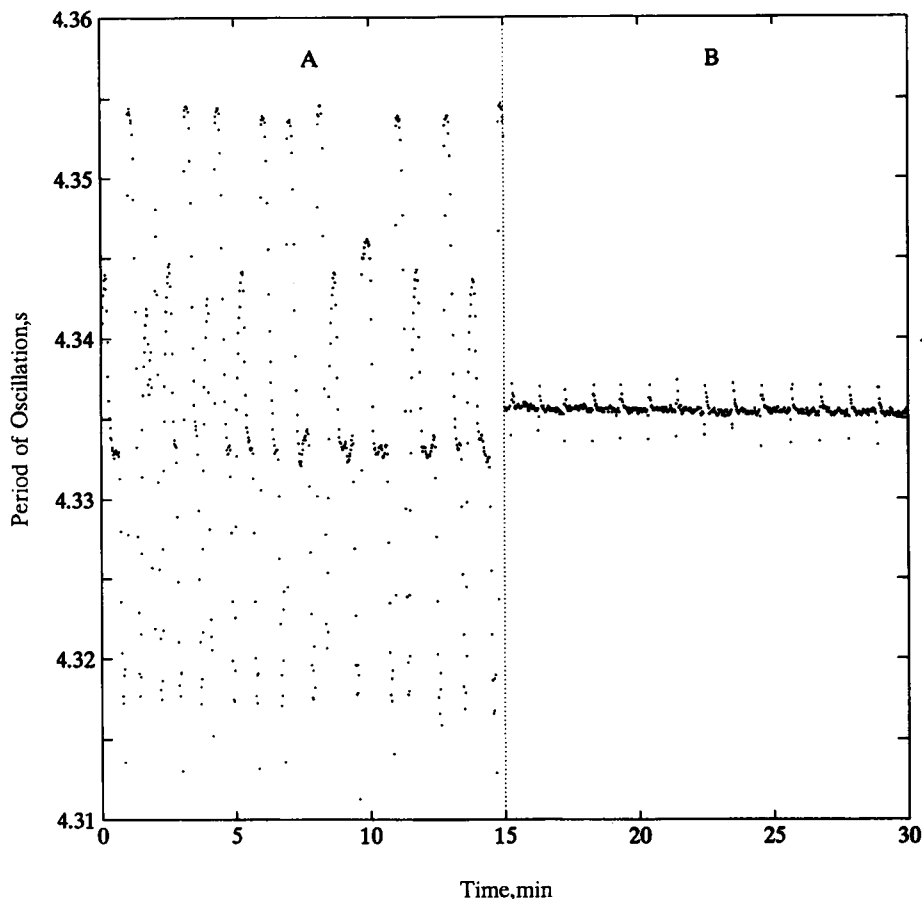
Figure 4   *(continued from the previous page)*

mer and polymer, respectively, which can be estimated through the following relationships:

$$\frac{1}{\rho_M} = \sum_{j=1}^{NM} \frac{x_j}{\rho_{M_j}}, \quad \frac{1}{\rho_P} = \sum_{j=1}^{NM} \frac{y_j}{\rho_{P_j}} \qquad (3)$$

where NM indicates the number of monomer species and x_j and y_j the weight fractions of the jth component in the overall amounts of monomer and polymer in the reactor, respectively. These composition values are readily evaluated from the overall amounts of residual monomer (M_j) and produced polymer (P_j) of each component as follows:

$$x_j = \frac{M_j}{\sum\limits_{k=1}^{NM} M_k}, \quad y_j = \frac{P_j}{\sum\limits_{k=1}^{NM} P_k} \qquad (4)$$

Substituting eqs. (4) and (3) in eq. (2), after some algebraic manipulations, the following equation is obtained, where both monomer conversion and composition are involved:

$$\rho = (w + e + i + 1) \times \left[\frac{w}{\rho_W} + \frac{e}{\rho_E} + \frac{i}{\rho_I} \right.$$

$$\left. + \sum_{j=1}^{NM} \frac{x_j^0}{\rho_{P_j}} + (1 - X) \sum_{j=1}^{NM} x_j \Delta v_j \right]^{-1} \qquad (5)$$

where x_j^0 indicates the weight fraction of the jth monomer in the monomer mixture initially charged into the reactor and $\Delta v_j = 1/\rho_{M_j} - 1/\rho_{P_j}$. According to eq. (5), a linear relationship between conversion and specific volume $(1/\rho)$ of the emulsion is obtained only in the case where no composition drift (i.e., change of x_j) arises during the reaction.

In the general case, the application of eq. (5) for estimating on-line conversion from density data requires the on-line knowledge of the polymer composition in the reactor. This can be obtained experimentally, for example, through gas chromatography measurements of suitable samples taken from the reactor during the batch. In this case the delay in updating the composition values x_j in eq. (5) is determined by the duration of the sampling procedure
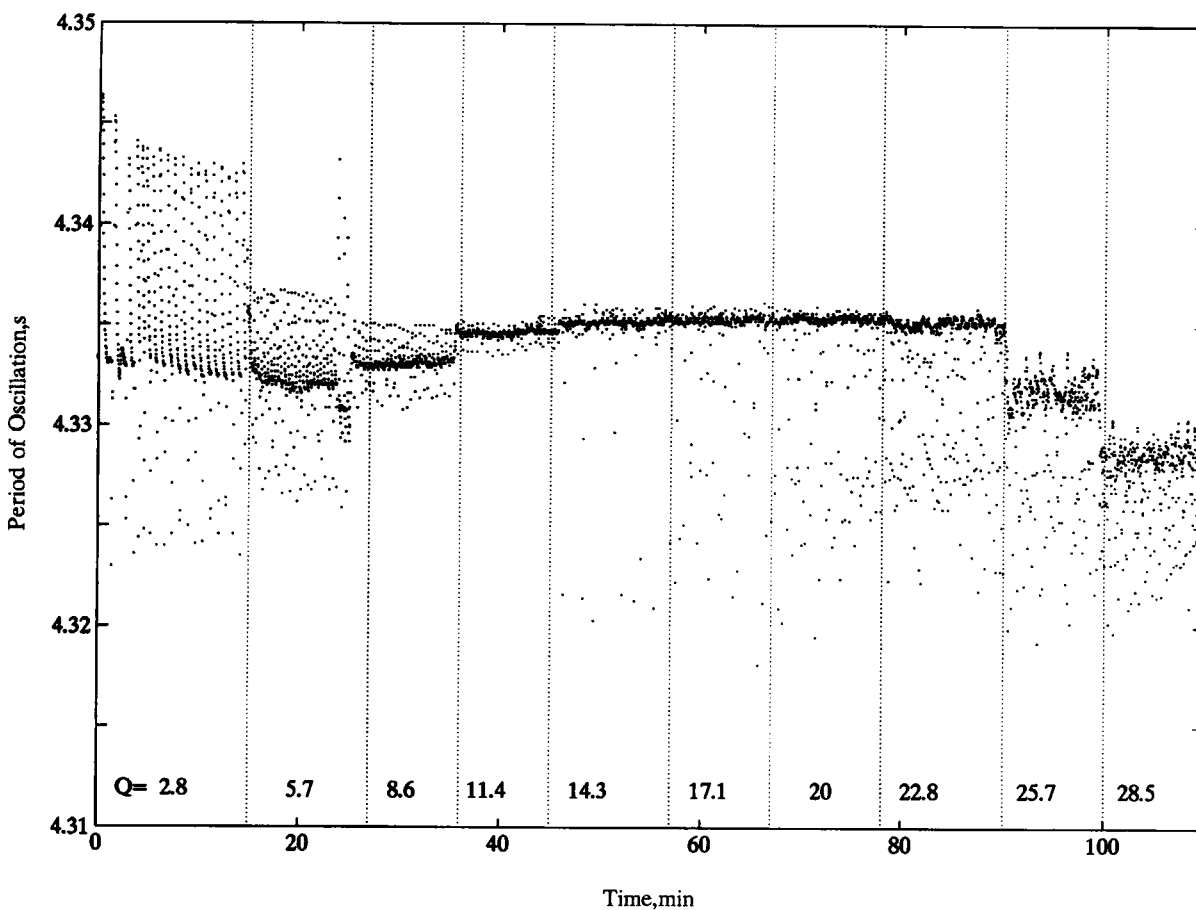
Figure 5 Recorded T values vs. time for different sample flow rates. Q values in g/min.

and of the gas chromatographic analysis. If the characteristic time of the reaction batch is large enough with respect to such a delay, then the pro-

cedure above leads to sufficiently accurate conversion values. Alternatively, the composition evolution in emulsion copolymerization systems can be esti-

Table II   Reaction Recipes[a]

Run	Monomer (g)		w (g/g)	e (g/g × 10²)	i (g/g × 10²)	Flow Rate (g/min)
3*	STY	100	6.0	2.00	0.40	14.3
14*	STY	90	6.7	4.17	1.05	14.3
17	STY	90	6.7	4.17	1.05	14.3
20	STY	90	6.7	6.67	1.05	14.3
21*	MMA	90	6.7	4.17	1.05	14.3
22	MMA	90	6.7	4.17	1.05	14.3
26	MMA	90	6.7	4.17	1.05	5.7
27	MMA	90	6.7	2.07	1.05	5.7
28	MMA	90	6.7	1.04	1.05	8.6
30*	MMA	27	6.7	4.17	1.05	14.3
	STY	63				
38*	MMA	41	6.7	4.17	1.05	14.3
	ACN	96				
56	MMA	30	10.0	4.00	1.50	14.3
	VAC	70				

[a] Temperature = 50°C.
* Without preliminary monomer distillation.

mated through suitable models.[13,14] In this context, it is convenient to adopt models which predict polymer composition as a function of conversion rather then of time. This is because such models are much simpler and require only two classes of parameters: the reactivity ratios and those regulating monomer partitioning among all the involved phases. Since reliable values of all these parameters are available in the literature for many systems, these models can be used in the purely predictive mode, that is, without preliminary fitting of any adjustable parameter on experimental data. Since it has been shown[13] that these models provide rather accurate predictions of the composition evolution, the procedure based on such predictive models has been adopted in this work.

Finally, it is worthwhile mentioning that, in the case of systems where all monomer species and homopolymers exhibit the same density values (i.e., $\rho_{Mj} = \rho_M$ and $\rho_{Pj} = \rho_P$ for $j = 1$, NM, the emulsion density becomes independent of composition and eq. (5) reduces to the homopolymer relationship (2).

RESULTS

Nine homopolymerization and three copolymerization reactions have been performed, according to the recipes summarized in Table II. For each experimental run, more than 2,500 density values per hour have been recorded, from which the corresponding conversion-time diagrams have been obtained directly through eqs. (2) or (5) without adopting any filtering technique.

Homopolymerization

Let us first examine the case of styrene (STY) homopolymerization (runs 14, 17, and 20), whose measured conversion-time curves are shown in Figure 6 together with the points representing the conversion values measured off-line through gravimetry. Some fluctuations of the measured conversion data, due to monomer droplets, are present, particularly when operating with low concentration values of emulsifier (runs 14 and 17). For increasing values
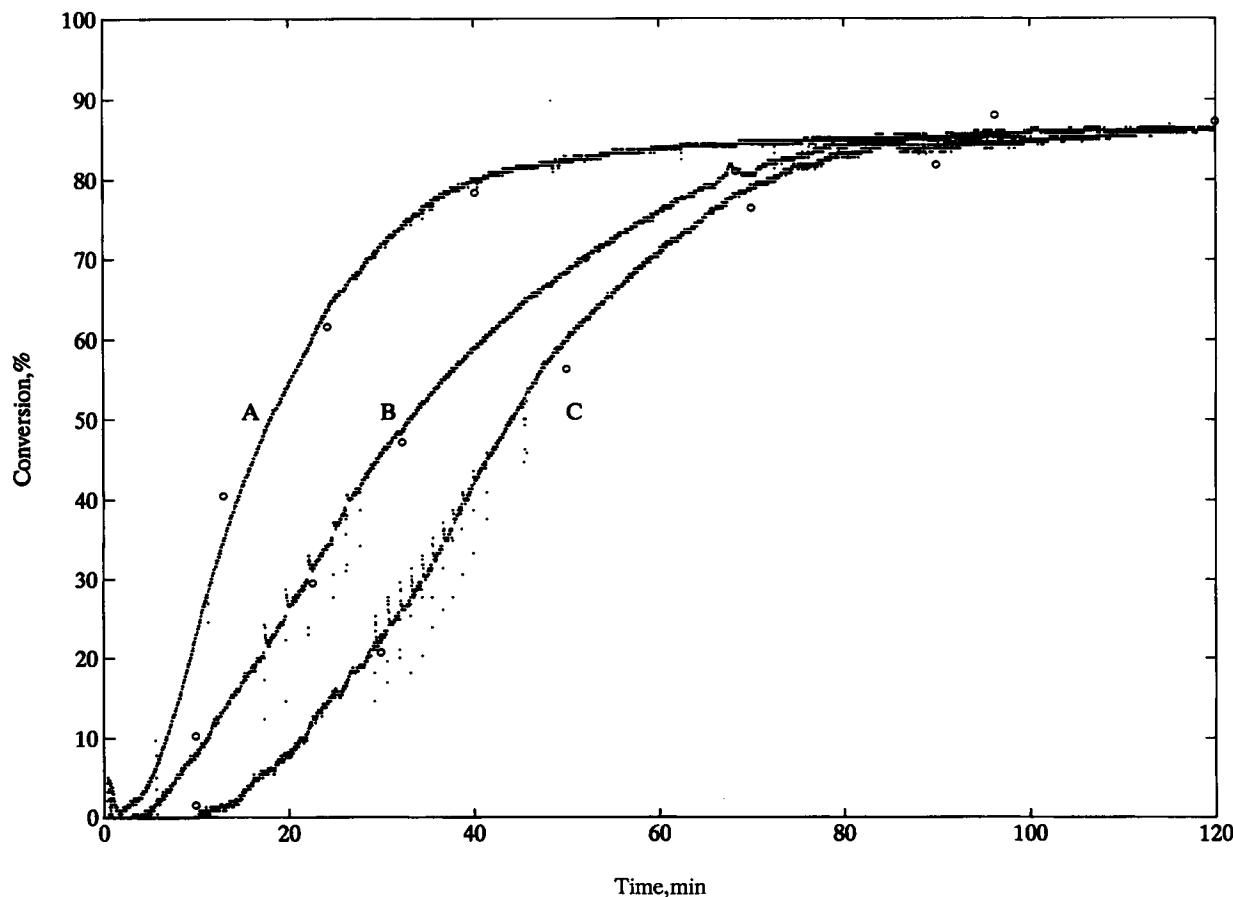

Figure 6   Conversion vs. time; runs 20 (A), 17 (B) and 14 (C) of Table II (O = data from gravimetry).

of the emulsifier concentration the scattering in the data decreases substantially (run 20). Note that runs 14 and 17 have been performed with the same recipe, the only difference being the adopted preliminary monomer purification. In particular, in the first case the reactant has been used without any preliminary purification while, in the second one, the monomer has been distilled just before the reaction so as to remove the inhibitor (tertbutyl-cathecol). By inspection of the corresponding conversion–time curves, it can be observed that the adopted inhibitor can be considered as an ideal one because it increases the time at which the reaction starts without affecting the rate of polymerization during intervals I and II (the curves can be superimposed by shifting the time scale).

In the case of MMA homopolymerizations (runs 26, 27, and 28), the obtained conversion-time curves are compared with the values (points) measured through gravimetry in Figure 7. It appears that the rate of polymerization can undergo an autoacceler-

ation phenomenon (the so-called "gel effect"), which is particularly strong when operating at low values of emulsifier concentration as in run 28, where the initial emulsifier concentration is very close to the critical micellar concentration. During this run, the density measurements have been interrupted because of pump failure due to polymer scale after about 30 min, thus warning against the use of this technique in the case of latexes with low stability. As in the case of STY, the role of the inhibitor (hydroquinone) usually adopted to stabilize the MMA monomer has been examined. Again, the monomer has been fed to the reactor with (run 26) and without (run 21) preliminary distillation, while adopting the same reaction recipe. In this case, a nonideal inhibiting action of hydroquinone is evidenced, as indicated by significant discrepancies arising in the reaction rate values through the entire experimental run.

In both cases (STY and MMA), the relative calibration procedure has been adopted. In particular,
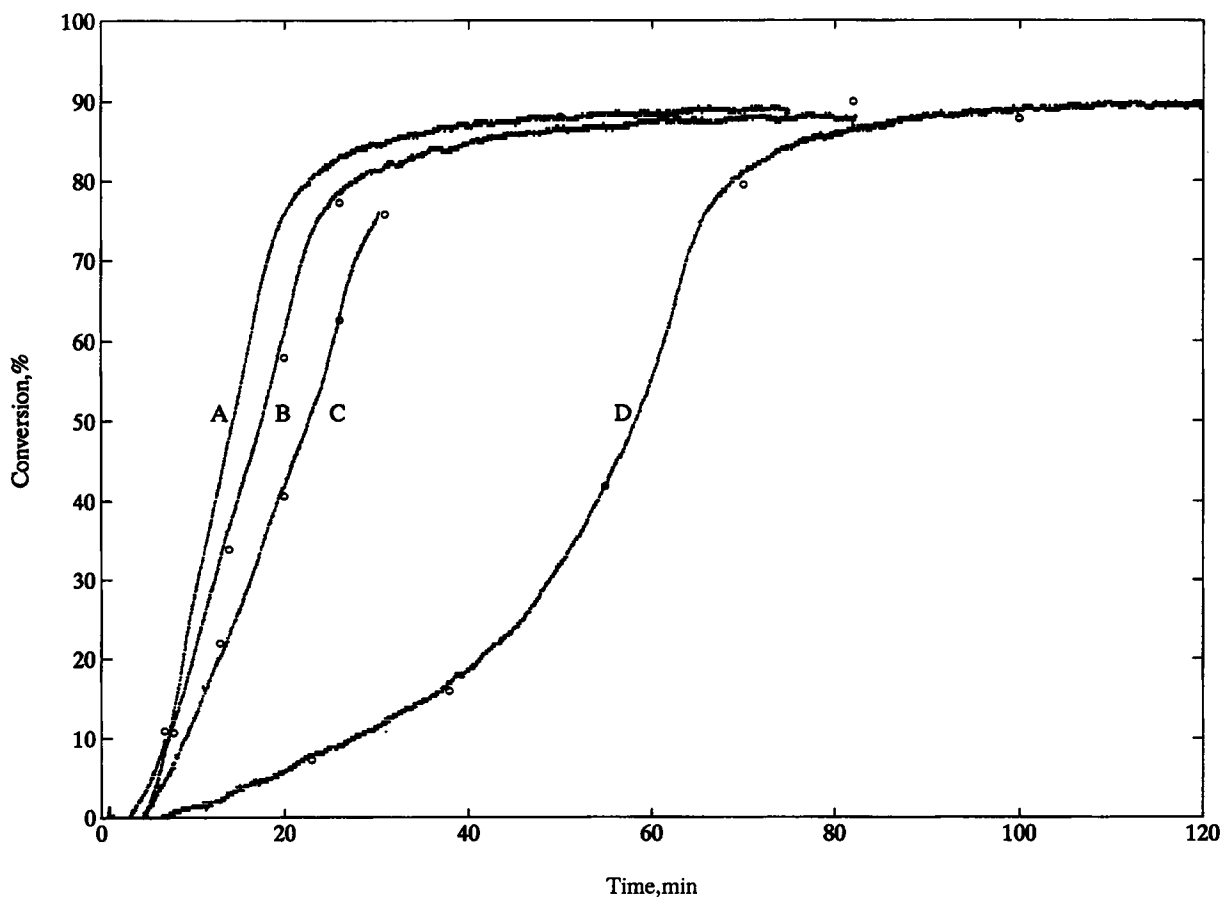

Figure 7   Conversion vs. time; runs 26 (A), 27 (B), 28 (C) and 21 (D) of Table II (O = data from gravimetry).

Table III   Adopted Values of Parameters[a]

	STY	MMA	VAC	ACN
		Densities (g/cm^3)		
ρ_M	0.906	0.910	0.930	0.806
ρ_P	1.05	1.17	1.07	1.17
		Reactivity Ratios		
STY		0.52		
MMA	0.46	1	0.03	1.35
VAC		26.0		
ACN		0.18		
		Water Solubilities (mol/L)		
	0.27×10^{-4}	1.59×10^{-4}	2.4×10^{-4}	7.35×10^{-4}

[a] Water density = 0.988 g/cm^3; $\phi^*_{VAC/MMA}$ = 0.8.

the monomer and polymer density values at 50°C summarized in Table III have been used in eq. (2), while the contributions of both emulsifier and ini-tiator have been neglected due to the low values of e and i. The following values of instrument calibration constants have been obtained: A = 0.08732 and
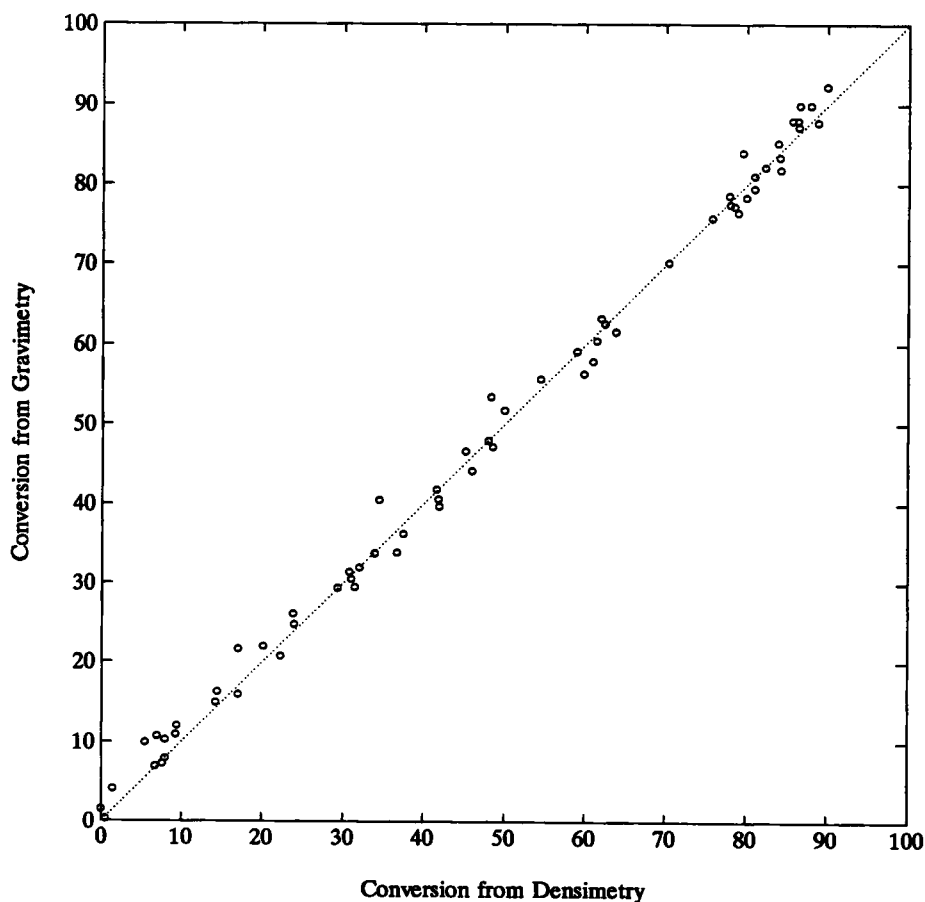

Figure 8   Comparison between conversion measurements obtained through gravimetry and densimetry in homopolymerization systems.

B = 7.50239 for STY, and A = 0.11739 and B = 10.46981 for MMA. After the preliminary calibration reaction run, these values of the instrument constants have been kept unchanged for all the following reactions.

In Figure 8 are compared the conversion values measured through the examined technique and through off-line gravimetry in all the experimental run referring to homopolymerization summarized in Table II. It appears that the agreement between the data obtained by the two procedures is satisfactory in the entire range of conversion values.

The importance of flow rate selection in the sampling circuit is further confirmed by the experimental results shown in Figure 9, with reference to the homopolymerization of MMA (runs 22 and 26). The same recipe has been adopted in the two experimental runs, which differ only in the value of the flow rate of the sample fluid in the densitometer cell (cf. Table II). Accordingly, such a variable is responsible for the anomalous behavior exhibited by run 22, as can be justified through the following arguments. Despite the presence of the phase separator, very small gas bubbles (or "microbubbles"), which are formed in the reactor, enter the densitometer cell. During the reaction the free emulsifier is depleted, and, then, the dimension of these bubbles decreases. Therefore, it may happen that the sampling flow rate provides a residence time in the phase separator, which is sufficient for eliminating all the bubbles initially present in the reactor, but not the smaller ones which are formed later on during the reaction. This is what happened in the experimental run 22 (sampling flow rate = 14.3 g/min), whose conversion–time curve, as shown in Figure 9, is identical to that obtained in run 26 (with lower sampling flow rate = 5.7 g/min) up to a conversion value equal to about 75%, where it starts to deviate and exhibit a strongly anomalous behavior. It is worth stressing that such a behavior is highly reproducible and that microbubbles are so small to be hardly seeable. This phenomenon has to be carefully considered because, although "macrobubbles" (whose dimension is comparable to the diameter of
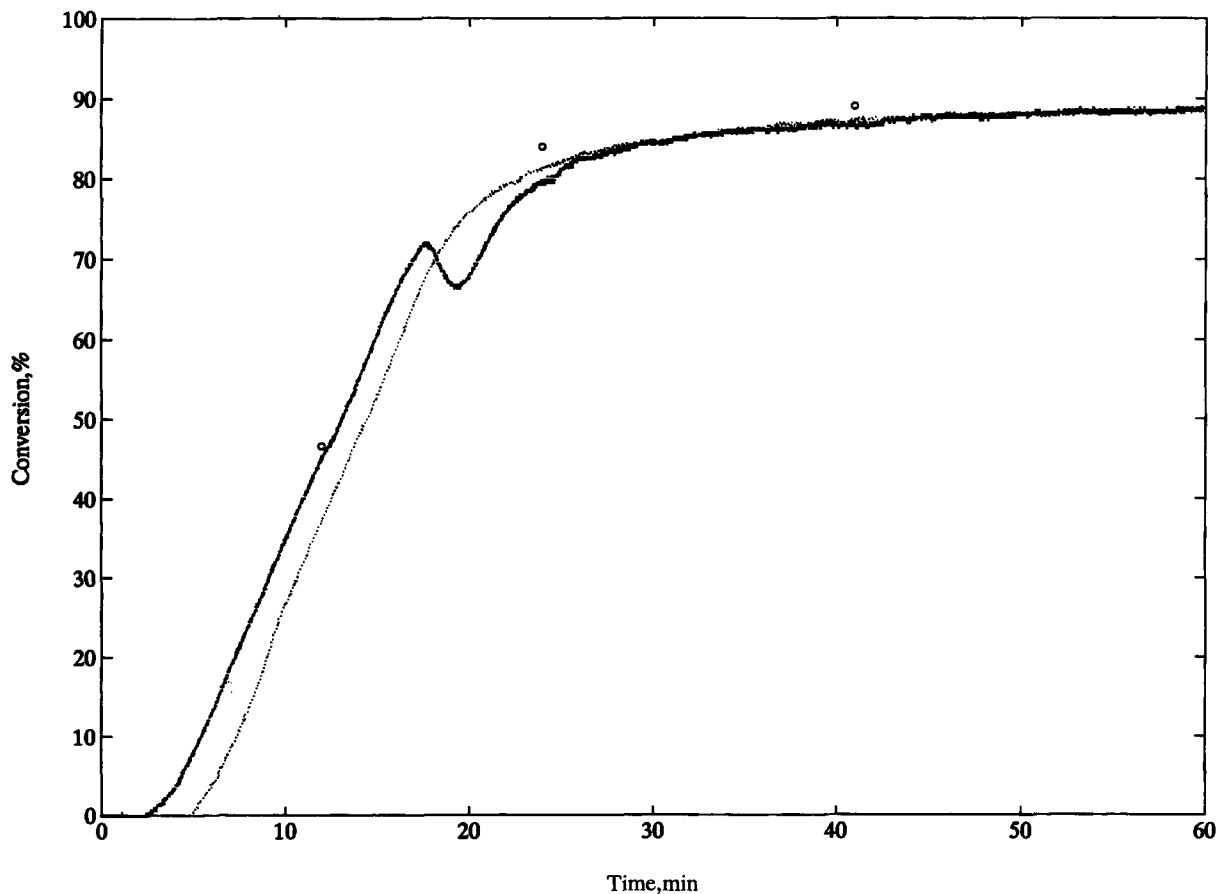

Figure 9   Conversion vs. time; runs 22 and 26 (dotted) of Table II.

the U-tube in the densitometer cell) cause a rather evident macroscopic scattering in the data (cf. Fig. 5), these microbubbles are much smaller and then produce a fictitious decrease of emulsion density, which in turn produces estimates of conversion lower than the true value, but without any macroscopic scattering. In conclusion, the value of the sampling flow rate has to be selected within a range of values which, as illustrated in Figure 5 in the case of STY, allows one to account for the influence of both droplets and macrobubbles; however, the lower values within this range should be preferred so as to minimize the danger of disturbances due to microbubbles formed during the reaction.

The experimental technique described above allows one to record the time evolution of the polymer conversion in a discrete way, but with a frequency such that it can be regarded as a continuous signal with respect to the characteristic time of the reaction (cf. Figs. 6 and 7). Thus it is possible to obtain reaction rate estimates by numerical differentiation of the collected conversion values. This would be a rather useful information, since the knowledge of the reaction rate provides the basis for elucidating the kinetics of the various phenomena involved in an emulsion polymerization reactor.

As expected, the differentiation procedure enhances local oscillations or discontinuities in the conversion data. Accordingly, the collected conversion data have been smoothed through the following simple procedure:

$$F_i = \frac{\sum\limits_{k=0}^{L} X_{i+k-L/2}}{L + 1} \qquad (6)$$

where X_i is the conversion value corresponding to the ith measurement provided by the densitometer, F_i is its filtered value, and L is the even number of conversion values, centered around X_i, which are used in the averaging procedure. The rate of the reaction is estimated through numerical differentiation of the filtered values F_i according to the following expression:

$$F'_i = \frac{F_{i+N/2} - F_{i-N/2}}{N \, \Delta t} \qquad (7)$$

where Δt indicates the time interval between two subsequent measurements ($\simeq 1.4$ s) and $N \, \Delta t$ is the time interval considered in the numerical differentiation. The values of both L and N can be tuned for each particular examined system by trial and

error. In particular, $L = 86$ for STY and $L = 44$ for MMA have been found able to eliminate the faster oscillations without significantly affecting the reliability of the estimated reaction rate values. The time interval used in the differentiation (7) has been tuned with respect to the characteristic time of the reaction, so as to lead in both the examined cases to a value of one tenth of the duration of the reaction interval II.

The obtained conversion rate values, F'_i as a function of time and conversion are shown in Figure 10(a) for STY (runs 17 and 20) and in Figure 11(a) for MMA (runs 26, 27, and 28). Note that, in order to help further considerations, in Figures 10(b) and 11(b) show the conversion values where the transition between the classical Smith–Ewart reaction intervals II and III occurs. According to simple material balances, the conversion value corresponding to the disappearance of the monomer droplets can be estimated as 45% and 31% in the case of STY and MMA, respectively.

From the observation of the conversion rate versus conversion curves reported in Figures 10(b) and 11(b), a few interesting considerations arise. First, it appears that a maximum occurs in some instances during the first two intervals—a feature anticipated in previous experimental works (cf. Min and Ray[15]) but not clearly evidenced. In particular, it appears that the rate of polymerization decreases during reaction at larger values of the emulsifier concentration while it increases at lower ones. Finally, at larger conversion values, i.e., within interval III, the so called "gel effect" is clearly evidenced. The autoacceleration is larger in the case of MMA than in the case of STY. Moreover, it is confirmed that the importance of this phenomenon is larger for smaller values of the emulsifier concentration and, therefore, for larger particle size [Fig. 11(b)].

It is worth stressing that it would be difficult to obtain this kind of experimental information through a classical discrete technique of conversion measurement such as gravimetry or gas chromatography. In this respect, the performance of on-line densimetry seems comparable to that of the calorimetric technique developed by Moritz.[10]

Copolymerization

First, the behavior of a typical copolymer system that does not require to account for composition changes in estimating conversion by means of densimetry is shown in Figure 12 in terms of conversion as a function of time (run 30 of Table II). This is
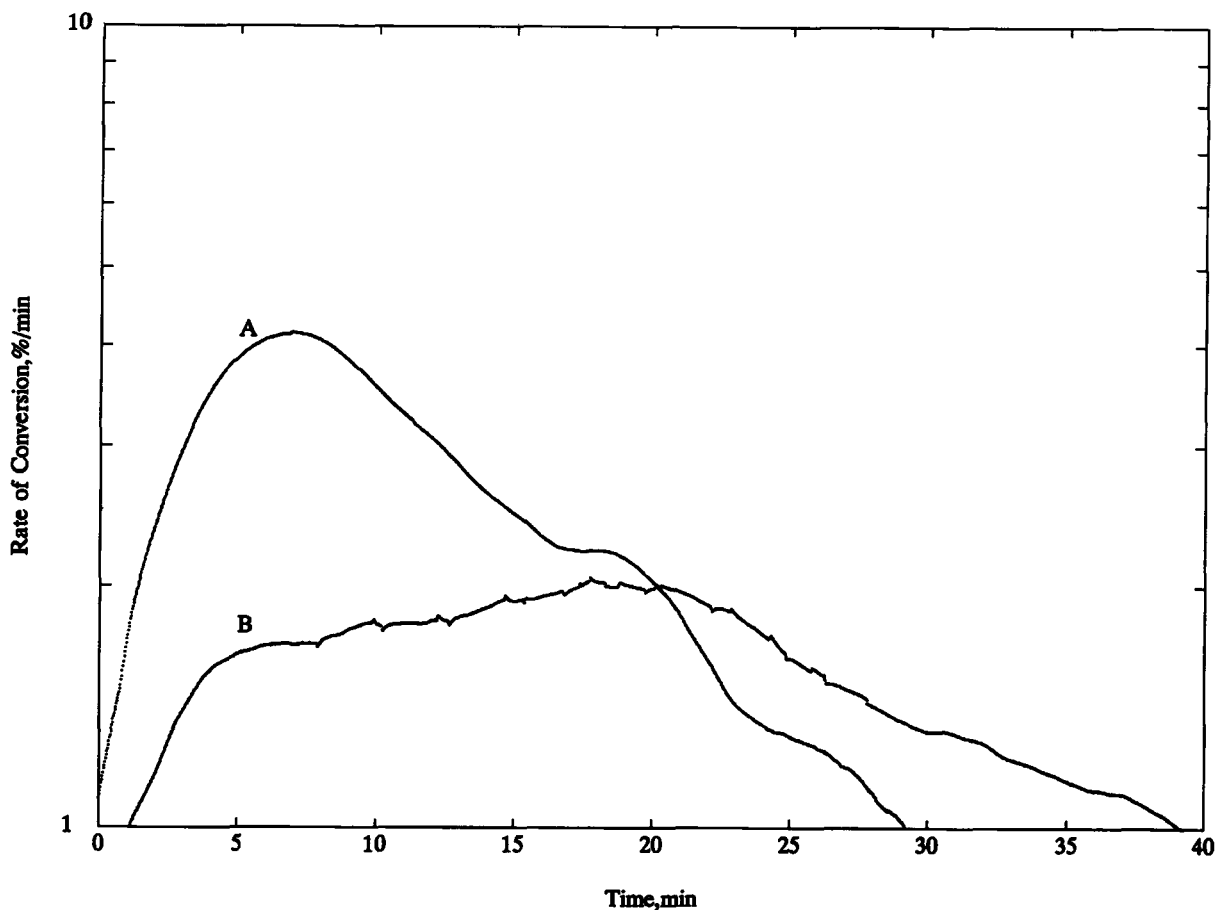
Figure 10 Polymerization rate vs. (a) time and (b) conversion; runs 20 (A) and 17 (B) of Table II.

constituted by STY and MMA, whose monomer and polymer densities are very similar [i.e., $\Delta v_1 = \Delta v_2$ in eq. (5)]. Moreover, the overall compositions of both monomer (x) and polymer (y) do not change significantly during the batch reaction.[13] Accordingly, eq. (2) has been used, with constant values for the densities ρ_P and ρ_M. Note that the same approach has been adopted with respect to instrument calibration, where, according to the relative calibration procedure described above, the composition corresponding to the final conversion value determined through gravimetry has been assumed equal to the initial one. The following values of the instrument constants have been estimated: $A = 0.10180$ and $B = 9.13307$. On the whole, from Figure 12 it appears that the agreement between conversion values estimated through gravimetry and densimetry is satisfactory.

Next, two different systems characterized by a significant composition drift have been examined: ACN–MMA and VAC–MMA (runs 38 and 56 of

Table II). As described above, it is necessary to account for the changes of the overall composition of both monomer and polymer so as to properly evaluate conversion through eq. (5). This has been accomplished through suitable composition-conversion models.[13,14] In particular, the model described by Storti et al.[14] has been used in the purely predictive mode, that is, using numerical values of the involved parameters taken from the literature, as summarized in Table III. The reliability of the model, previously proved through extensive comparison with experimental data for the systems STY–MMA and ACN–MMA,[13] has been confirmed also for the third system VAC–MMA by a preliminary "ad hoc" experimental analysis. The obtained results are summarized in Figure 13, where the predicted residual monomer composition vs. conversion curve is compared with the experimental data obtained through gas chromatography and gravimetry, respectively. Similarly as in the previous case, also for the VAC–MMA system, a good agreement be-
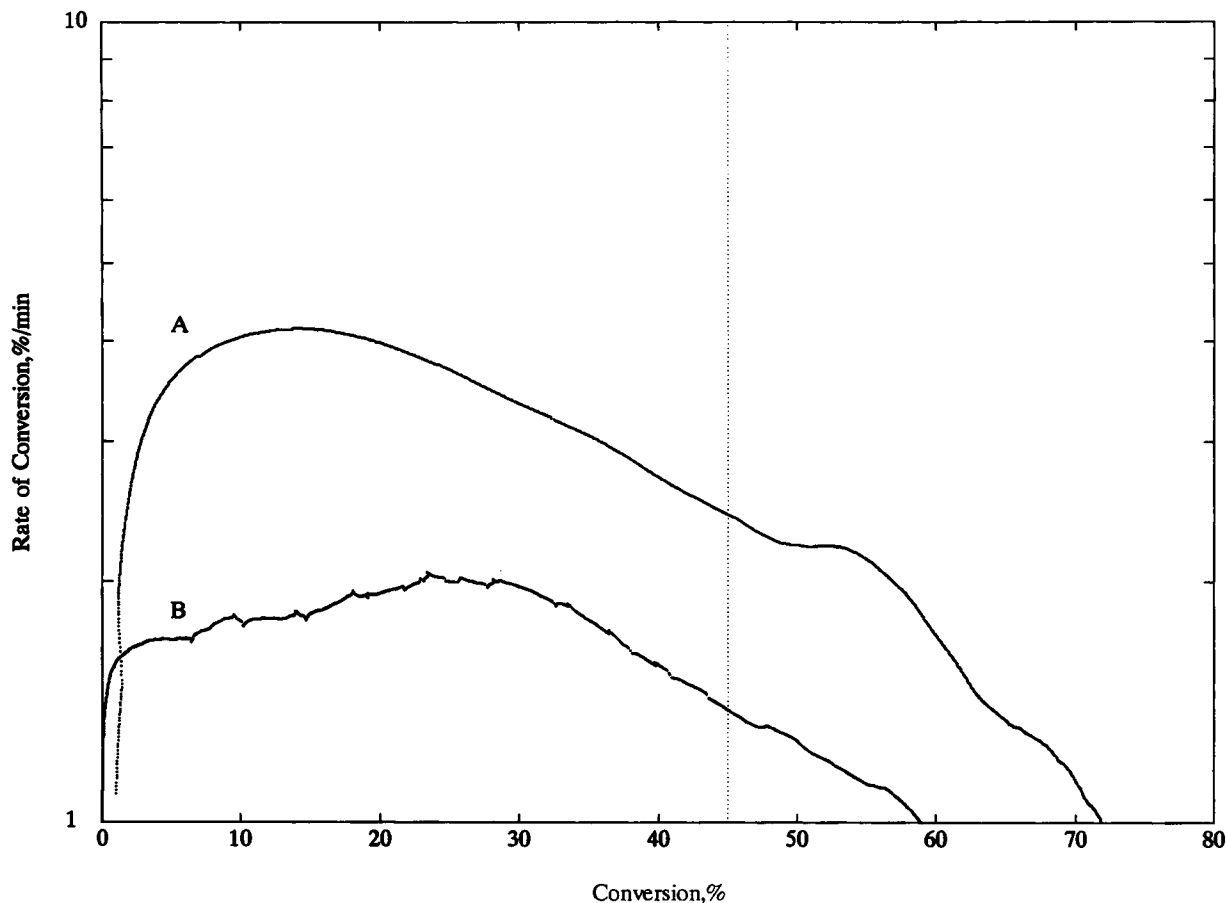
Figure 10 (*continued from the previous page*)

tween the calculated curves and the experimental data is obtained without any parameter adjustment. In conclusion, the unknown conversion value corresponding to each density measurement obtained through the densitometer is calculated by coupling eq. (5) with the composition–conversion relationship given by the model.

Note that the same approach has been adopted in the relative calibration procedure, where the composition value corresponding to the final conversion is needed. The following values of the instrument constants have been estimated: $A = 0.12200$ and $B = 10.79447$ for ACN–MMA; $A = 0.09423$ and $B = 8.36995$ for VAC–MMA.

The estimated conversion-time curves are compared in Figures 14 and 15, in the case of ACN–MMA (run 38) and VAC–MMA (run 56), respectively, with the conversion values (points) obtained through independent off-line gravimetry. Good agreement between the conversion values obtained through densimetry and gravimetry is observed in the whole range of conversion values.

Finally, as a comparison, it is worthwhile evaluating the inaccuracies which would be introduced in the estimation of conversion if one would ignore the composition changes in the reacting system. The conversion values estimated in this case through the densitometer are shown in Figures 14 and 15 (dotted curves). Such values have been obtained using again eq. (5), but assuming a constant composition value equal to that of the monomer mixture initially introduced in the reactor. Note that the same values of the instrument constants, A and B, previously used when estimating conversion through densimetry coupled with composition–conversion modeling, have been kept in this case. From the comparison of the conversion values estimated with (continuous curve) and without (dotted curve) the conversion–composition model, it appears that significant errors in the estimated conversion-time curve are introduced when neglecting the composition drift for systems where the monomer and polymer densities of the involved components are different, as in the case of ACN–MMA and VAC–MMA.
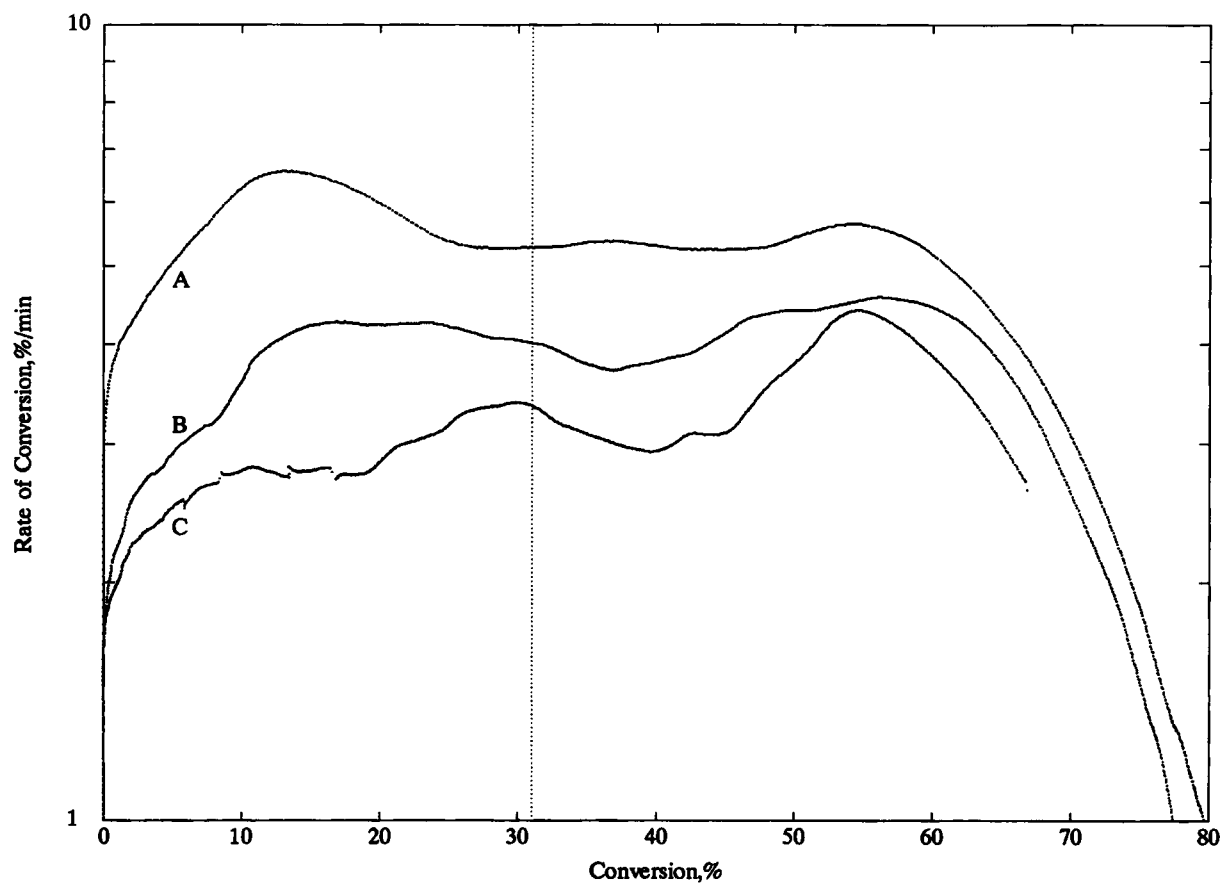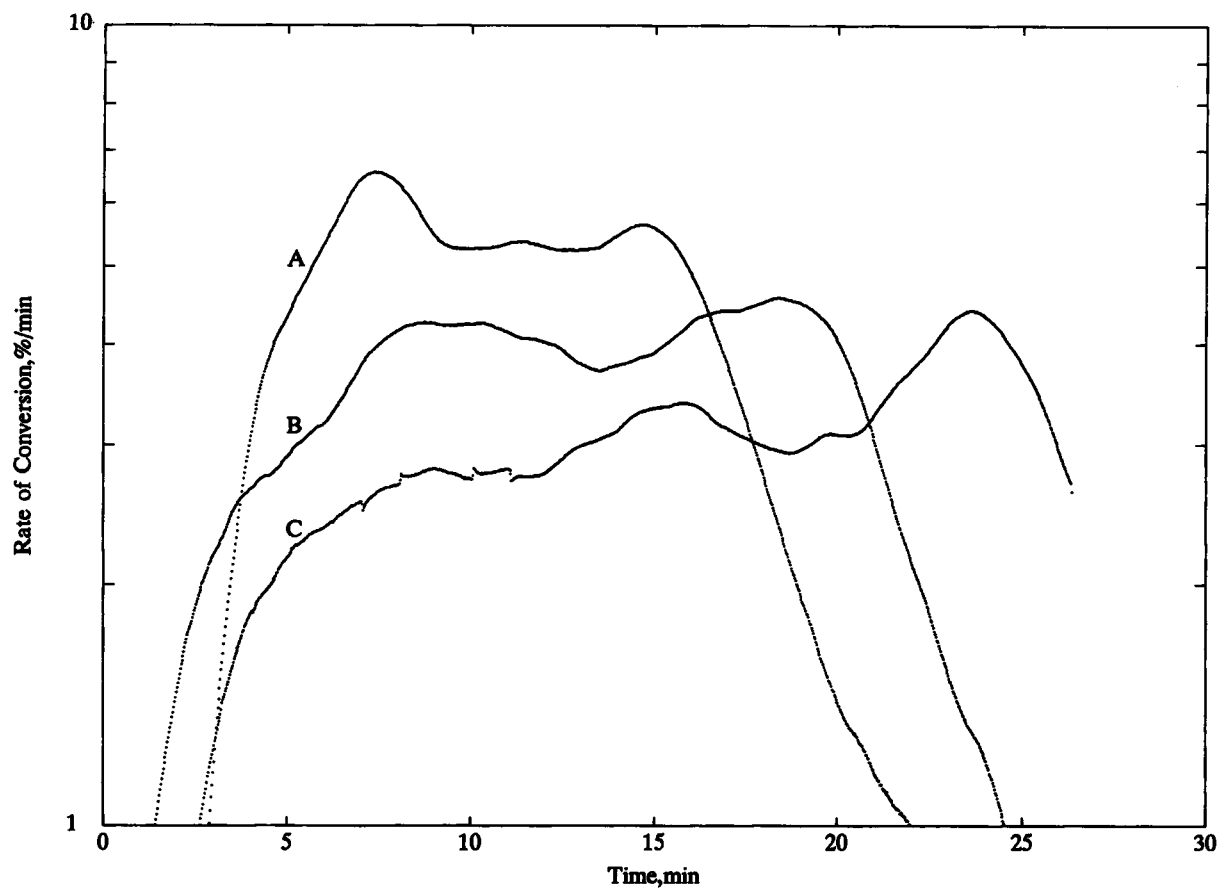
Figure 11 Polymerization rate vs. (a) time and (b) conversion; runs 26 (A), 27 (B), and 28 (C) of Table II.
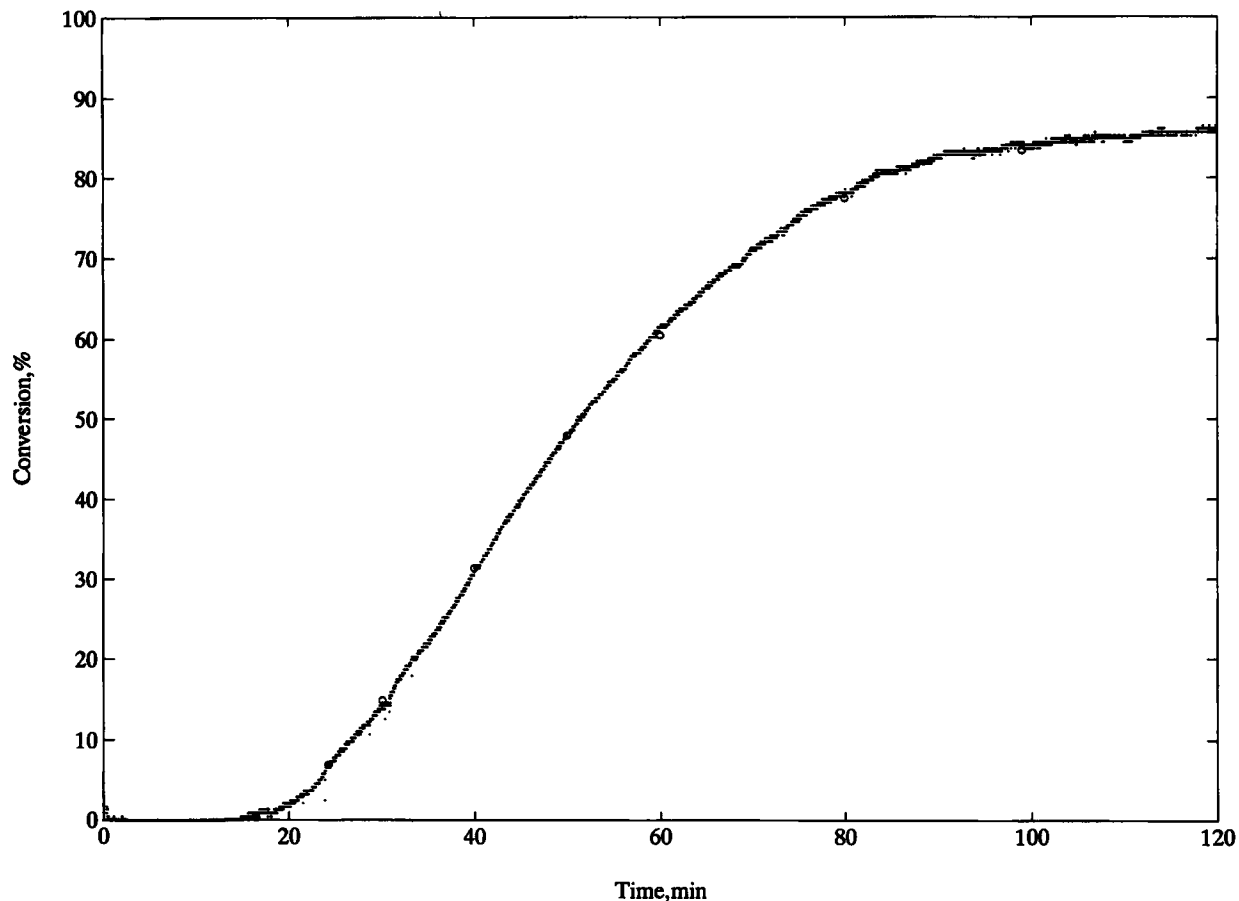
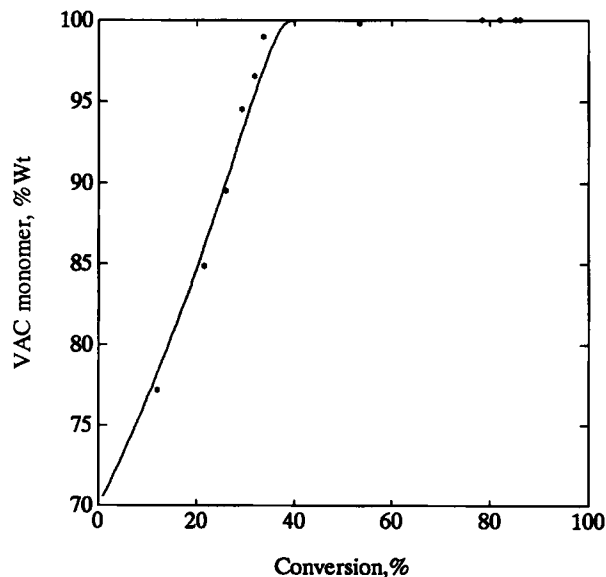**Figure 12**   Conversion vs. time; run 30 of Table II (O = data from gravimetry).

Figure 13   Composition vs. conversion; run 56 of Table II.

CONCLUSION

Densimetry is a suitable technique for on-line monitoring of conversion in emulsion homopolymerization and copolymerization reactors. In the case of copolymerization systems, where composition changes during the reaction and the monomer and polymer densities are different, the density measurements need to be coupled with the value of the reacting system composition. This can be conveniently provided by a predictive composition-conversion model. The obtained on-line conversion measurements appear to be reasonably accurate (about ±1.5%) in the whole range of conversion values.

The on-line conversion estimation requires operating the densitometer under flowing conditions of the polymer latex sample. The reliability of the so-obtained density measurements is significantly improved through suitable modifications in the tub-
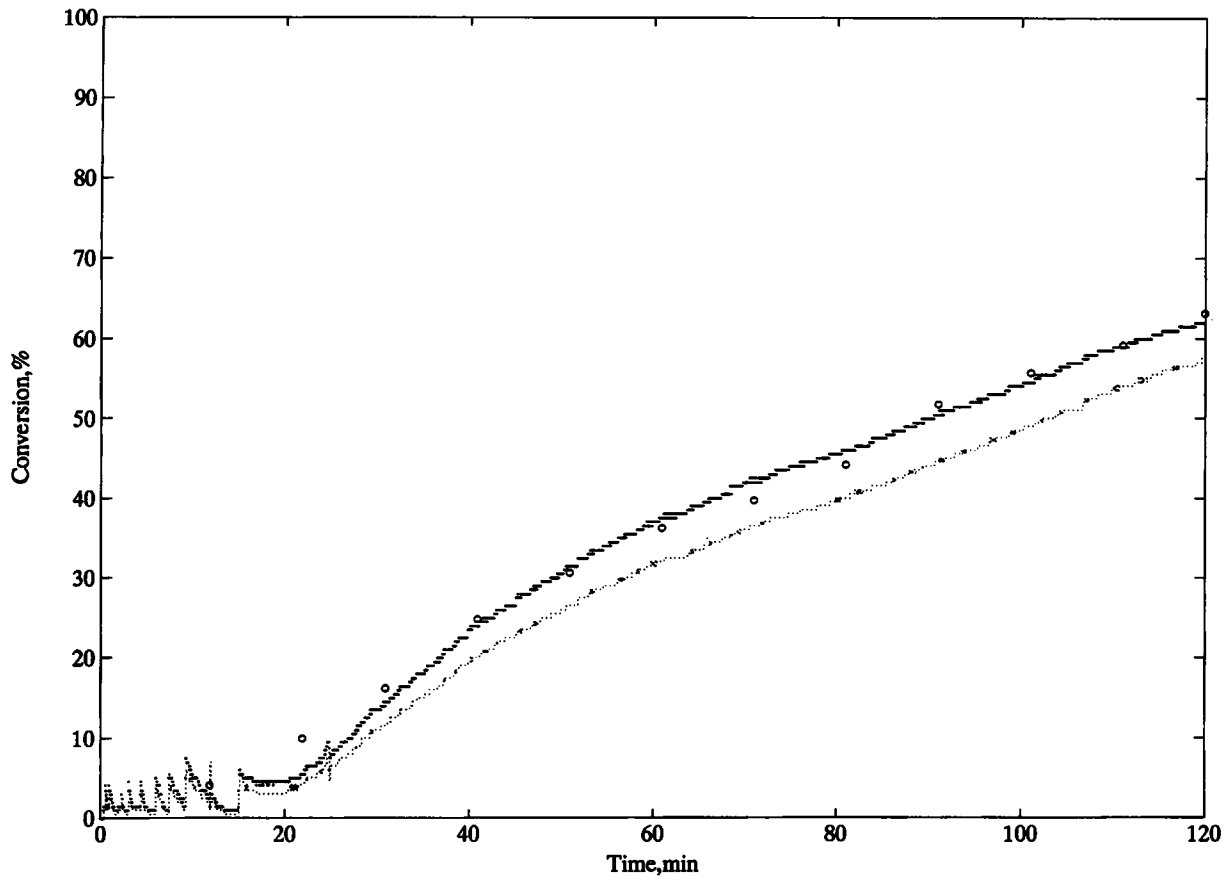
Figure 14   Conversion vs. time; run 38 of Table II (O = data from gravimetry).
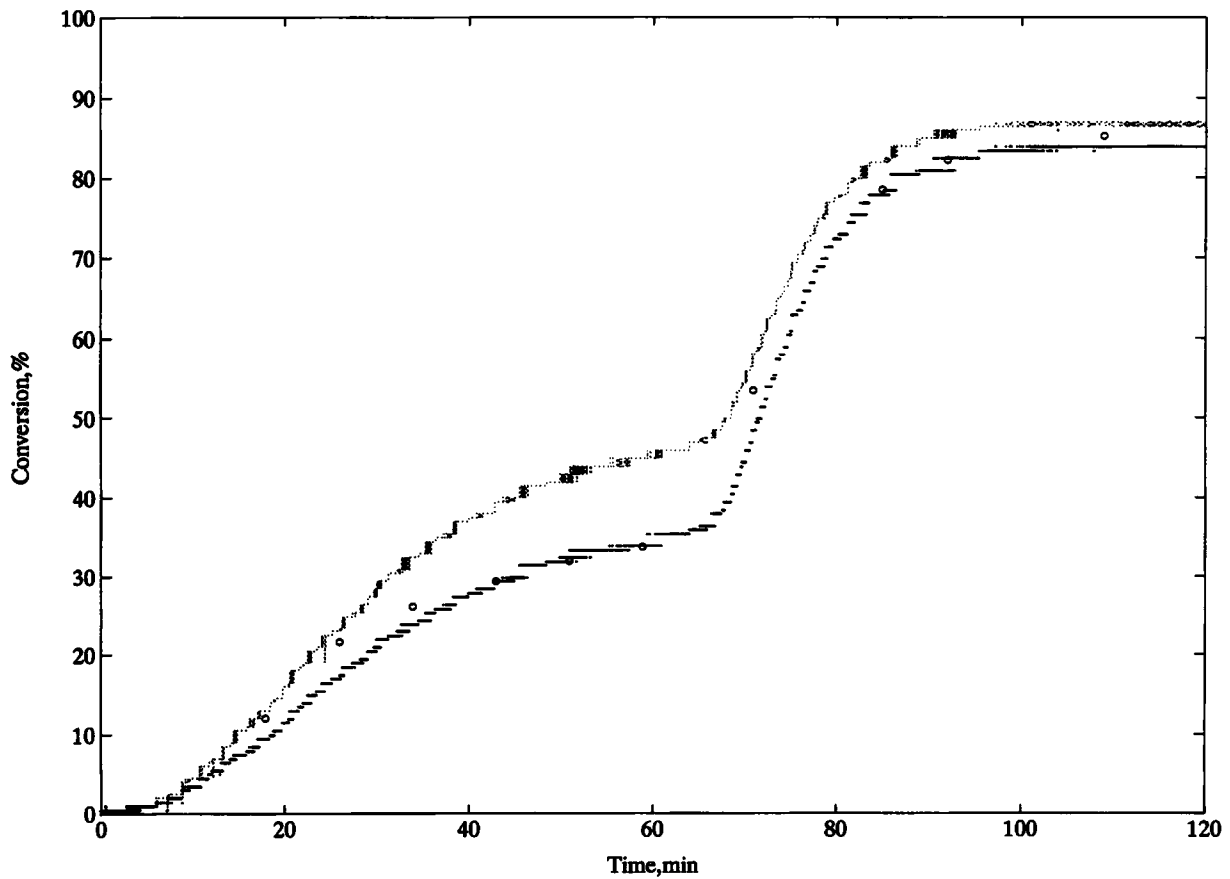

Figure 15   Conversion vs. time; run 56 of Table II (O = data from gravimetry).

ing of the sampling circuit, proper calibration of the instrument, and an accurate selection of the sample flow rate. The latter variable controls the presence of monomer droplets and gas bubbles in the measurement cell, which are responsible for the occurrence of disturbances in the obtained measurements.

NOMENCLATURE

A	densitometer calibration constant defined by eq. (1) $(g/cm^3/s^2)$
B	densitometer calibration constant defined by eq. (1) (s^2)
e	ratio between the initial amount of emulsifier and the initial amount of monomer (g/g)
F_j	filtered value of the jth conversion measurement (g/g)
i	ratio between the initial amount of initiator and the initial amount of monomer (g/g)
L	number of data for averaging
M	overall amount of monomer (g)
M_j	amount of the jth monomer (g)
N	number of time intervals for numerical differentiation
NM	number of monomer species
P	overall amount of polymer (g)
P_j	amount of monomer j units in copolymer (g)
Q	sample flow rate (g/min)
Δt	sampling interval (s)
T	period of oscillation (s)
W	amount of water (g)
w	ratio between the initial amount of water and the initial amount of monomer (g/g)
X	weight conversion (g/g)
x_j	overall weight fraction of the jth monomer (g/g)
y_j	weight fraction of monomer j units in copolymer (g/g)
ρ	emulsion density (g/cm^3)
ρ_j	density of the jth component, (g/cm^3)
Δv_j	specific volume variation for the jth component between monomer and polymer $(= 1/\rho_{Mj} - 1/\rho_{Pj})$ (cm^3/g)

Subscripts and Superscripts

E	emulsifier
I	initiator
M	monomer
P	polymer
W	water
0	initial
$'$	time derivative
i, j, k	indices

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