On-Line Gas Chromatography and Densimetry to Obtain Partial Conversions of Both Monomers in Emulsion Copolymerization

LILIAN F. J. NOËL,* ERIC C. P. BROUWER, ALEX M. van HERK, and ANTON L. GERMAN†

Department of Polymer Chemistry and Technology, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

SYNOPSIS

Monitoring and controlling composition drift is an important issue in emulsion copolymerization. Due to the heterogeneity of the polymerization system often combined with nonideal kinetics, predicting copolymer composition and changes in feed composition as a function of time is not straightforward. Therefore, accurate and fast on-line determination of partial conversions of the separate monomers is a key to understanding and controlling the copolymer system studied. For this reason on-line densimetry, resulting in overall weight conversion, is combined with on-line gas chromatography, resulting in the overall ratios of the residual monomer. Combining these two on-line data gives the partial conversion of each monomer as a function of time without the need of an internal standard. The determination of partial conversion of monomers in batch emulsion copolymerization from on-line gas chromatography and on-line densimetry is illustrated for the monomer system methyl acrylate-vinyl acetate. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Composition drift is an aspect typical of (emulsion) copolymerization resulting in chemically heterogeneous copolymers. Monitoring and controlling the occurrence of composition drift is extremely important because copolymer properties strongly depend on, among others, the chemical heterogeneity of the product. Prediction of copolymer composition and changes in the composition of the reaction mixture as a function of time is often hampered by nonideal circumstances or the lack of parameters needed for model predictions. Therefore, accurate and fast on-line determination of partial conversions of the separate monomers is of great importance.

The use of on-line densimetry in obtaining conversion data for homopolymerizations is already well established. Successful applications have been re-

ported for the polymerization of methyl methacrylate (MMA),[1-3] vinyl acetate (VAc),[4-6] styrene (St),[7] and even for the gaseous monomer butadiene.[8] Apart from the butadiene work that fitted the densimetry data with gravimetry results at the end of each reaction, all other experiments were based on the assumption that the volumes of monomer, polymer, and water are additive. Further, it is assumed that the specific volume of the (co)polymer is a linear function of the homopolymer specific volumes. As a consequence the specific volume of heterogeneous and homogeneous copolymer of the same overall copolymer composition is assumed to be equal. Using these assumptions in combination with prerun data of the total density difference going from 1 to 100% conversion, the on-line density signal can be transformed into an on-line conversion signal. Note that because conversion determination is based on calibration techniques or prerun data, it is a relative method rather than an absolute one.

For copolymerization reactions the use of on-line densimetry becomes more complex because composition drift will lead to changing specific volumes of the monomer and polymer phase. Nevertheless,

---

some attempts have been made to monitor batch emulsion copolymerizations using a densimeter. One of the first attempts was made by Abbey[1] for the monomer combination butyl acrylate (BA)–MMA. Abbey made a rough estimation of the resulting conversion–time curve for the BA–MMA emulsion copolymerization by simply neglecting the occurrence of composition drift although he knew that this would lead to a skewed conversion–time plot. Canegallo et al.[7] recently monitored emulsion copolymerizations by densimetry for the monomer systems St–MMA, acrylonitrile–MMA, and VAc–MMA. They accounted for composition drift by modeling this phenomenon and taking into account the effect on density of changing monomer and polymer compositions as a function of conversion. In order to obtain conversion from densimetry data Canegallo et al.[7] calculated the calibration constants from a prerun based on the theoretically calculated begin and end densities. Although they were able to transform density into conversion data not only for homopolymerization but also for copolymerization, care should be taken that the density cell is calibrated at the same temperature and flow conditions as during the reaction to ensure that correct and absolute density values are obtained. The calibration constants used by Canegallo et al.[7] were determined using density values of polymer and monomer at the reaction temperature, although the temperature in the density cell was approximately 6°C lower. This indicates that, although they were able to convert density into conversion successfully, the density values obtained were not absolute.

Monitoring the partial conversion of both monomers as a function of time in emulsion copolymerization instead of modeling the phenomenon, as Canegallo et al.[7] did, can only be performed if additional information is available to convert density data into partial conversion data. This extra information must be related to either the monomer ratio or the copolymer composition.

Accurate ratios of residual monomers can be obtained by gas chromatography (GC). GC of the liquid phase is a well-established method to obtain overall monomer ratios in an emulsion system. Successful liquid phase on-line GC applications have been reported by Rios et al.[9] and van Doremaele.[10] Alternatively, on-line head space analysis of the gas phase above the reactor content can be an option,[11] although this method is not straightforward because it involves the knowledge of monomer partitioning behavior between the reaction mixture and the gas above it, under the relevant reaction conditions. The complete characterization in terms of absolute con-centrations of both monomers as a function of time during emulsion copolymerization, employing exclusively GC analysis, is only possible when using an internal standard or a constant injection volume. However, the addition of an internal standard to the reaction medium can influence polymerization kinetics and monomer partitioning[12] leading to different conversion–time curves. Further, the internal standard will remain in the product. Accurate and reproducible injection volumes can only be obtained by taking relatively large samples from the reaction mixture. Because injecting these large samples directly into the GC column leads to overload of the column and the use of a splitter does not give reproducible absolute amounts of monomer, an approach has to be used in which an internal standard must be added to the sample, followed by sample dilution and injection in the GC. It is obvious that this method can only be applied on-line if expensive robotics are included in the system. In the approach presented herein the on-line GC is used only to obtain the overall *ratio* of the monomers present in the batch emulsion copolymerization, thus avoiding the complications of using an internal standard or a constant injection volume.

Combining on-line GC and on-line densimetry is then required to obtain *absolute* monomer concentrations of both monomers as a function of time. The use of this new combination of on-line techniques, in principle, should allow fast monitoring and control of composition drift.

THEORY

Calculation of conversion based on density data obtained by on-line densimetry is mostly based on the volume additivity assumption.[1-5,13] When this assumption is valid, the monomer conversion is a linear function of the specific volume of the emulsion. In these cases the conversion can be calculated with[2]

$$x = \frac{v_e^o - v_e^t}{v_e^o - v_e^1} = \frac{\dfrac{1}{\rho_e^o} - \dfrac{1}{\rho_e^t}}{\dfrac{1}{\rho_e^o} - \dfrac{1}{\rho_e^1}} \tag{1}$$

where: x, v (cm^3/g), and ρ (g/cm^3) stand for the conversion, specific volume, and density, respectively; subscript e stands for the total emulsion; and superscripts o, t, and 1 stand for the conversion at the beginning of the reaction, time t, and complete conversion, respectively. Note that the specific vol-

ume equals the reciprocal density value for each component. The initial and final specific volumes of the reaction can be determined experimentally from a prerun or they can be approximated as weighted averages of the component specific volumes:

$$\nu_e^o = x_m \nu_m + x_s \nu_s \qquad (2a)$$

$$\nu_e^1 = x_m \nu_p + x_s \nu_s \qquad (2b)$$

where x stands for mass fraction and the subscripts m, p, and s stand for monomer, polymer, and serum (the aqueous phase), respectively. Note that the initial mass fraction of monomer in the reaction equals the mass fraction of polymer at complete conversion. The density values (i.e., reciprocal specific volumes) of the monomers and polymers used herein are listed in Table I.

EXPERIMENTAL

Materials

The following materials were used for emulsion copolymerization reactions: reagent grade St (Merck, Darmstadt, Germany); reagent grade MA and reagent grade VAc (Janssen Chimica, Tilburg, The Netherlands); doubly deionized water; sodium persulfate (NaPS, p.a., Fluka AG, Buchs, Switzerland) as initiator; sodium dodecyl sulfate (SDS, Fluka AG) as surfactant; and sodium carbonate (Na$_2$CO$_3$, p.a., Merck) as buffer. Before use, the St, MA, and VAc were distilled under reduced pressure to remove inhibitor. The middle fraction was cut and stored at 4°C. The calibration of the density cell for on-line measurements was performed with doubly deionized water and toluene (p.a., Merck).

Emulsion (Co)polymerization

The batch emulsion (co)polymerization reactions were performed in a 1.3 dm^3 stainless steel reactor fitted with four baffles at 90° intervals and a six bladed turbine impeller. In Figure 1 the configuration of the batch reactor system with on-line densimeter and on-line gas chromatograph is given. The reaction volume in the sampling loops is approximately 21 cm^3, which normally is about 2% of the total reaction volume. Because this volume is divided over two loops and the flow through each membrane piston pump is about 11.7 cm^3/min, it takes approximately 1 min for a small sample volume to pass the loop for on-line measurements. Considering this relatively small sample volume and the short resi-

Table I Density Values of Ingredients Used in Emulsion (Co)polymerizations at Reaction Temperature 50°C

Ingredient	Density (g/cm^3)	
	Monomer	Polymer
Styrene	0.8781	1.0438
Vinyl acetate	0.8935	1.1696
Methyl acrylate	0.9186	1.1987
Water[15]	0.9881	
Toluene[14]	0.8375	

dence time in the sampling loop, the density and monomer ratio values obtained from on-line measurements are assumed to be similar to the conditions in the reactor itself. Further, all effects of possible different reaction rates (due to lower temperatures in the sampling loop) of the emulsion mixture in the sampling loop as compared with the reaction mixture remaining in the reactor, are assumed to be of negligible influence on the total reaction mixture in the reactor. The recipes of the emulsion homo- and copolymerization reactions are depicted in Table II. The St and VAc homopolymerizations and the MA–VAc copolymerization were performed under nitrogen at 50°C. Previous to the addition of the initiator solution, the rest of the reaction mixture was stirred at ca. 800 rpm to ensure a relatively homogeneous reaction mixture. At the moment of addition of the initiator solution the on-line monitoring is started. All reactions were monitored by gravimetry and on-line densimetry yielding conversion-time curves. The copolymerization reaction was also monitored by GC (both on-line and off-line) providing the overall monomer fractions as a function of time. Combining both data gives the overall conversion of both monomers at the moment of sampling.

Densimetry

The measuring principle of a densimetry instrument is based on the change in the natural frequency of a vibrating U-shaped sample tube filled with sample liquid or through which the sample fluid flows continuously. The relationship between the period of oscillation of the sample tube, T, and the density, ρ, is given by

$$\rho = \frac{1}{A} (T^2 - B) \qquad (3)$$

where A and B are the temperature dependent instrument constants determined by calibration with fluids (toluene[14] and water[15]) of known density. Off-line densimetry was performed using a thermostated Anton Paar DMA 10 density cell. The density of monomer or solutions can be calculated directly from the oscillation period of the sample tube and the calibration constants using eq. (3). The on-line measurements described here were performed using an Anton Paar DMA 512 density cell thermostated with an M3 LAUDA thermostatic bath and an Anton Paar DMA 60 Densimeter. The DMA 512 remote cell can be used for high pressure and high temperature applications. The U-tube is made of stainless steel with an internal diameter of 2.4 mm and with an internal volume of approximately 1 cm^3. A membrane piston pump was used for continuous transport of the reaction mixture through the on-line density cell. A preheater (length 15 cm, internal diameter 2 cm) was placed around the sampling tube just in front of the densimeter. The temperature of

Table II Batch Emulsion Polymerization Recipes for Homopolymerization (Homo) of St and VAc, and Copolymerization of MA–VAc

Ingredients (g)	Homo-St	Homo-VAc	MA-co-VAc
St	99.743		
MA			50.454
VAc		50.193	50.411
SDS	2.299	0.296	0.299
NaPS	1.904	0.201	0.212
Na$_2$CO$_3$	0.894	0.088	0.085
Water	1031.96	979.37	992.34

the bath was set at such a temperature (53.0 $\pm$ 0.1°C) that the reactor and the density cell were at the same temperature (50.0 $\pm$ 0.1°C). Contrary to the results of Canegallo et al.[7] the density–time curves obtained from on-line densimetry were not sensitive to large scatter of density values resulting
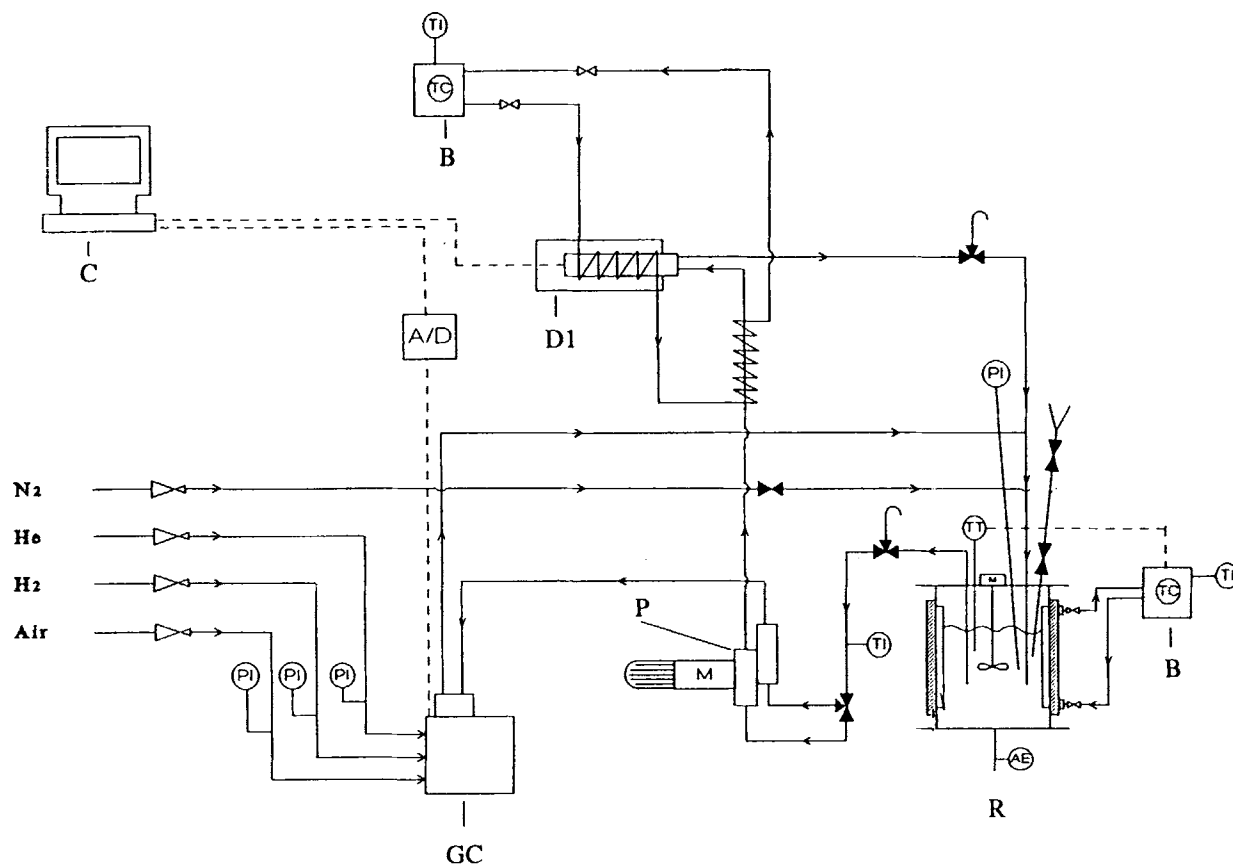

Figure 1 Schematic representation of the configuration for on-line monitoring batch emulsion copolymerizations using densimetry and gas chromatography. D1, on-line densimeter; GC, on-line gas chromatograph; B, thermostatic baths; R, reactor suited with baffles and a heating jacket; C, on-line computer; P, double membrane piston pump.

from the formation of gas bubbles or coalescence of monomer droplets in the U-tube. Therefore, in our setup no phase separator was installed.

GC

For on-line GC a Carlo Erba 8030 gas chromatograph was used, equipped with an extra heated zone in which the on-line injection system was installed. Continuous flow of helium for GC analysis and continuous flow of the reaction mixture through a sampling disc valve[16] (diameter sampling hole 1.56 mm; thickness disc 2.95 mm) was maintained during reaction. After the completion of each GC analysis a new reaction mixture sample with a volume of approximately 5.6 μL was injected into the GC apparatus by simply rotating the sample disc. The GC sampling valve could be operated either fully automatically by using a computer, or manually. The column used for on-line GC analyses was a J & C Scientific Capillary DB5 column with a length of 30 m, an internal diameter of 0.53 mm, and a film thickness of 1.5 μm. For the MA–VAc reactions consecutive samples could be taken every 3 min resulting in a sufficient number of values of overall monomer ratios as a function of time. The on-line GC values were compared to those obtained off-line to check the validity of the system used. For off-line purposes a Hewlett–Packard (HP) 5890A gas chromatograph was used in combination with an HP 3393A integrator, an HP 7673A automatic sampler, and a capillary chromopack CP-sil 19CB column (length 25 m, internal diameter 0.53 mm, film thickness 2 μm).

RESULTS AND DISCUSSION

Density

Theoretically the conversion can be calculated from density measurements without performing a prerun if the specific volumes (i.e., reciprocal densities) of the components in the three phases and mass fractions of the aqueous phase, the monomer phase, and the polymer phase are known. However, small errors in density will lead to large deviations in conversion determination for low solids reactions where the total density difference is small. Therefore, on-line conversion determination from densimetry without the use of prerun data can only be performed accurately if the measured density value is an accurate and absolute one. It should be noted that measuring absolute density in an on-line system as presented

herein is hampered by several complications. For instance, the density signal depends on flow rate through the density cell, temperature, "homogeneity" of the heterogeneous system (i.e., mixing to avoid phase separation in intervals I and II in emulsion polymerizations), and pressure. The influence of each individual parameter on the density signal depends on the sensitivity of the selected density cell toward these parameters. Extra complications will occur as the viscosity will change as a function of conversion because this may lead to changing flow rates and temperatures in the density cell. It should be noted that temperature control in the density cell is difficult due to slow heat transfer between the heating system and the U-shaped tube which is surrounded by a vacuum. Good temperature control can only be obtained by using a good preheater or using low flow rates. Conversion determination from absolute density values may be obtained if a flow controller is installed or by calibration of the density cell under a series of (flow) conditions. Using the experimental setup presented, the specific volume determined from on-line densimetry can deviate approximately 0.003 cm^3/g from the absolute specific volume as a result of flow effects, the accuracy of the measuring device, and scatter on the calibration constants. This implies that the method will result in accurate conversion determinations for high solids content emulsion polymerizations (40% solids; $\nu_e - \nu_o \approx 0.1$; 3% error on conversion determinations); for low solids content reactions large errors in conversion determination may occur (5% solids; $\nu_e - \nu_o \approx 0.01$; 30% error on conversion determinations). However, for two identical reactions where flow and temperature fluctuations are approximately equal, the error on the specific volume will be so small (<0.0005 cm^3/g) that the prerun data of the first reaction can be used for on-line determination of conversion in the second reaction. This can either be done by measuring the total density difference and assuming volume additivity [eq. (1)], calculation of the calibration constants using the theoretical initial and final densities,[7] using the aqueous phase density as a fitting parameter,[6] or calibration of the density data on conversion data.[8]

From the above discussion it can be concluded that as long as densimetry does not result in accurate absolute density values, the quantitative use of densimetry during a reaction is limited to reactions for which a prerun has been performed. This makes densimetry a very useful method of on-line monitoring of standard reactions, i.e., the method is extremely useful for industrial application, at least up to 30% solids content.[4] On-line densimetry always
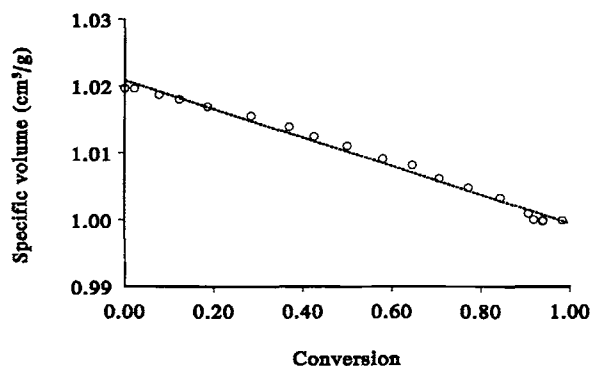
Figure 2 Comparison of experimental and theoretically linear (fitted) conversion-specific volume results for the batch homopolymerization of styrene.

Figure 3 Comparison of conversion results determined using on-line densimetry and gravimetry for the batch homopolymerization of styrene.

gives valuable qualitative information during a reaction, even if no direct information about absolute conversion is gained. Moreover, it is a very quick and accurate method to gather much data from an experiment because as soon as the reaction is finished, a complete and detailed conversion-time curve can be determined.

Homopolymerization

For batch emulsion homopolymerization reactions on-line densimetry is sufficient to monitor conversion as a function of time during the reaction. In the case of homopolymerizations, transforming density values into conversion values is straightforward [eq. (1)].

St

For St homopolymerizations the conversion-specific volume curve depicted in Figure 2 shows that the specific volume indeed is a linear function of the conversion of the reaction mixture. This justifies the use of eq. (1) to calculate conversion from the density data. Comparison of conversion–time data resulting from gravimetry and densimetry [using eq. (1)] shows acceptable agreement as can be seen in Figure 3. The bend in the density curve at 80% conversion is probably caused by fouling of the density cell. Although membrane piston pumps are known as low shear pumps, the use of this type of pump for on-line measurements of *ab initio* batch homopolymerizations of St may cause some pump plugging. Because this will influence the flow through the density cell and as a direct consequence the value of the calibration constants, pump plugging will directly affect the density–time curve resulting from on-line densimetry. Less plugging can be expected
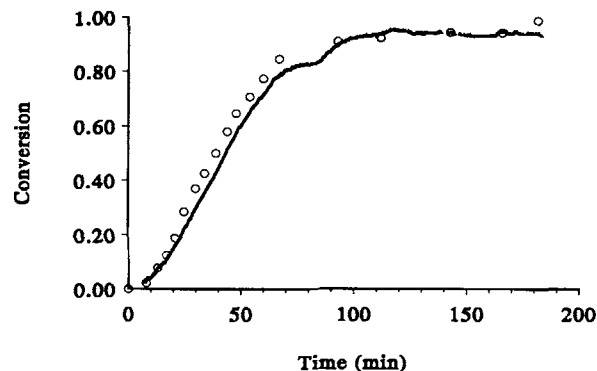
when using a peristaltic pump. However, finding proper tubing resistant to both monomers needed in emulsion copolymerization is difficult. Further, possible swelling of the tubes and deposit of polymer on the tubing will also affect the flow and therefore the calibration constants. Because monitoring emulsion copolymerization reactions is the main purpose of this setup, a membrane piston pump in combination with stainless steel tubing was selected.

VAc

The specific volume–conversion results for a VAc homopolymerization depicted in Figure 4 show clearly that not *one* single linear relationship exists between specific volume and conversion over the whole conversion range. This can only mean that the assumption of additive volumes is not valid for the emulsion polymerization of VAc, i.e., eq. (1) cannot be used. The deviating behavior is caused by volume contraction occurring when VAc is added to
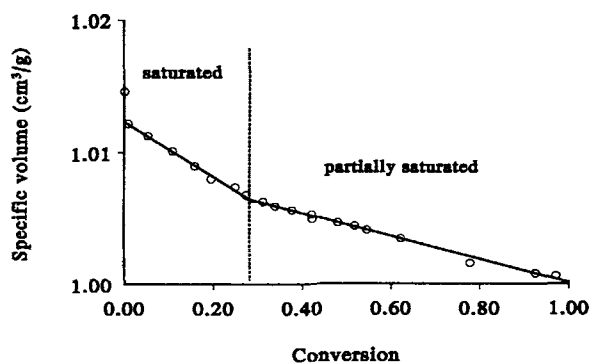

Figure 4 (O) Experimental conversion-specific volume results for the batch homopolymerization of vinyl acetate are fitted in two linear regions (saturated and partially saturated; solid lines).
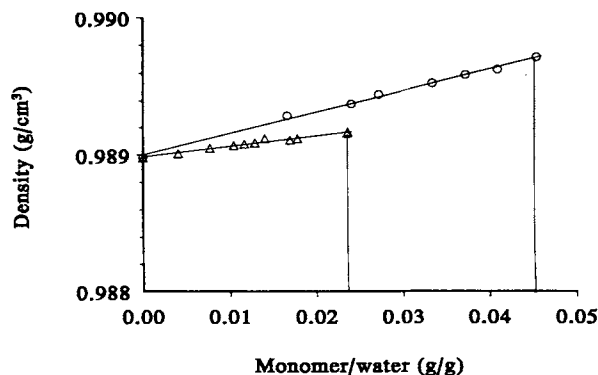
Figure 5 Experimentally determined density values for (△) VAc-water and (○) MA-water solutions as a function of the monomer/water ratio. The data are fitted with two linear relationships.

water. This volume contraction will lead to a density increase (instead of the expected decrease in case the volumes were additive) when VAc is added to water as can be seen in Figure 5 where the density of VAc-water solutions is depicted as a function of increasing amounts of VAc (increasing monomer/water ratios, M/W). All density values depicted in Figure 5 are below the maximum water solubility of VAc in water. Higher M/W ratios lead to a separate aqueous phase, saturated with monomer, and a separate monomer droplet phase. This immediately leads to phase separation and therefore to a huge scatter on the density values. Due to the linearity between density and M/W ratio, the solubility of VAc in water at 50°C can be determined from measuring the density of the saturated aqueous phase. This resulted in a water solubility for VAc of 0.28 mol/dm³. That the volume additivity assumption is not valid for other reasonably water soluble monomers either, is also illustrated in Figure 5 for MA. The water solubility of MA at 50°C resulting from density measurements is 0.55 mol/dm³. The kink in linearity shown in Figure 4 is primarily caused by the dissolved monomer in the aqueous phase. Due to the relatively high water solubility of VAc (0.28 mol/dm³) in combination with the relatively low M/W (0.051) used in the homopolymerization experiment (Fig. 4), a percentage of 48% of the VAc was dissolved in the aqueous phase at the beginning of the reaction. The difference between the one linear line and two linear regions situations will be smaller if a smaller percentage of the monomers is located in the aqueous phase, i.e., for higher M/W ratios and/or for monomers with lower water solubilities. This is illustrated by Penlidis et al.[4] who found reasonable agreement between gravimetry and densimetry conversion results for the batch emulsion

homopolymerization of VAc at a M/W ratio of 0.33 g/g (ca. 8% of the VAc is dissolved in the aqueous phase at the start of the reaction).

During the homopolymerization of VAc a substantial amount of the monomer will be located in the aqueous phase (48%). Using eq. (1) to calculate the conversion-time curve for this reaction will lead to a large difference between the conversion data, based on eq. (1), and gravimetry, as can be seen in Figure 6 (top line and triangles). These problems can be solved in three ways.

The first method is dividing the reaction into a saturated (interval II) and partially saturated (interval III) region. By doing so we can assume that we have two linear regions in which we can use eq. (1) again. For the presented VAc reaction the end of the saturation interval can be calculated based on the water solubility value (0.28 mol/dm³) and the swellability of monomer in the polymer phase (6.11 mol/dm³ swollen polymer phase) showing that interval II is ended at 26% conversion. The assumption of a linear region in the saturation region is quite acceptable because the total amount of VAc in the aqueous phase remains constant. Note, however, that by assuming a linear region in interval II, volume additivity between the polymer and the monomer in the swollen particle phase is assumed. For the partially saturated region the concentrations in both the aqueous phase and polymer particle phase will decrease. Deviations of the linear behavior will occur in this partially saturated region due to the fact that the aqueous phase is always closer to saturation than the polymer particle phase.[12] However, the results of this approach are quite acceptable as
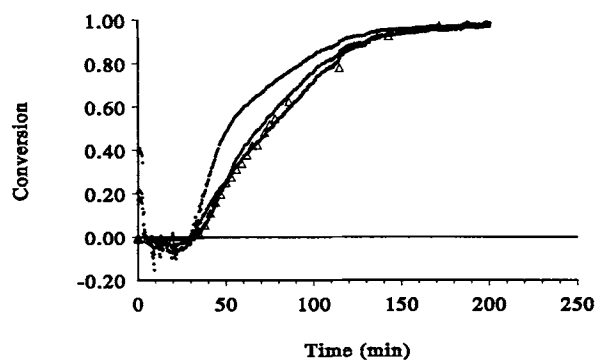

Figure 6 For the batch homopolymerization of vinyl acetate the calculated (three methods) and gravimetry based conversion-time curves are compared; calculation based on one (top line) and two (middle line) linear regions between conversion and specific volume; (△) gravimetry data; and calibration of on-line data using gravimetry results (bottom line).

can be seen by the reasonable agreement between the conversion–time curve resulting from this approach and gravimetry data (Fig. 6; middle line and triangles).

The second method is calibration of the density–time curve with a density–conversion relationship (fitted with a polynomial of the sixth power) obtained by comparing on-line density values with gravimetry results.[8] Using this approach accurate conversion–time curves can be obtained after calibration of the results or on-line by using the density–conversion relationship from a prerun. Using this approach excellent agreement between conversion–time curves resulting from densimetry and gravimetry is obtained (Fig. 6; bottom line and triangles).

The third method is determining the specific volume of the monomer in the three phases and adjusting eqs. (1), (2a), and (2b). However, again this approach only works if absolute densities are obtainable.

Conclusions About On-Line Densimetry in Emulsion Homopolymerization

In cases where more than approximately 5% of the monomer is dissolved in the aqueous phase at the beginning of the reaction, the volume additivity assumption cannot be used and the maximum water solubility of the monomer has to be taken into account.

Note that in cases where conversion information is needed at the end of the reaction, the calibration method is the most simple and accurate way to obtain conversion information because temperature and flow deviations, and water solubility effects are all accounted for as long as these phenomena are reproducible from one run to the other. Further, this method can be used in a similar way to obtain conversion data for emulsion polymerizations involving two or more monomers.
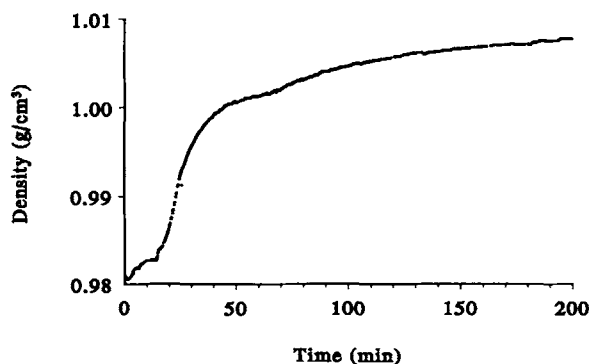
Figure 7 Density–time curve typical of the batch copolymerization of vinyl acetate with methyl acrylate.
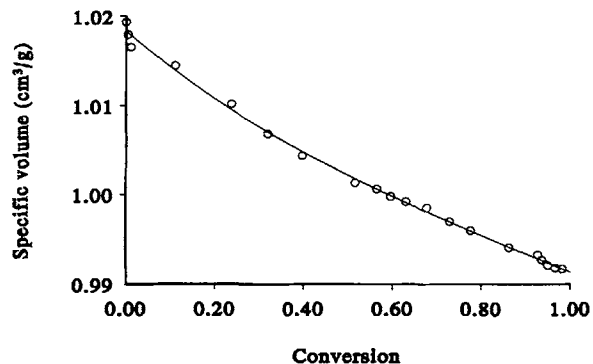
Figure 8 (---) Experimentally determined relation between specific volume and conversion for the batch copolymerization of MA–VAc; (O) conversion determined by gravimetry.

Emulsion Copolymerization of MA and VAc

In emulsion copolymerization reactions the monomer and copolymer compositions will also change as a function of conversion, probably leading to nonlinear conversion-specific volume curves (unless both monomers and polymers have similar densities). For the emulsion copolymerization of reasonably water soluble monomers such as MA and VAc, even more deviations from linearity of the conversion-specific volume curves can be expected. To avoid these problems the gravimetry calibration method described in the previous section is used to obtain accurate conversion–time curves.

A typical density–time curve resulting from on-line measurements of the batch emulsion copolymerization of MA and VAc is shown in Figure 7. Note that there is remarkably little scatter on the density data, even at the beginning of the reaction (interval II) where phase separation might occur. This can only be a result of the continuous pumping at turbulent conditions that prohibits phase separation in the density cell. It also must be mentioned that in case of VAc homopolymerization and MA–VAc copolymerization, hardly any pump plugging occurred during the reaction, i.e., a stable latex mixture is obtained. Transforming the density values into specific volumes and thereafter combining the specific volume–time values with conversion–time values obtained gravimetrically, results in a nonlinear conversion-specific volume relationship depicted in Figure 8. Using the relationship found by fitting the conversion-specific volume data, the specific volume values were transformed into conversion values (Fig. 9). Similar, on-line results can be obtained in case conversion is calculated based on the total difference in specific volume as a function of
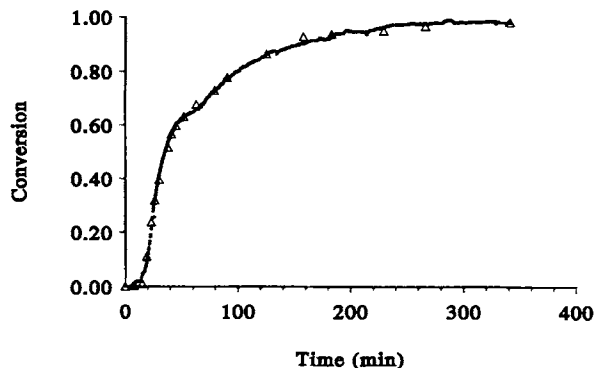
Figure 9   Conversion as a function of time determined (△) gravimetrically and calibrated using (○) densimetry for the batch copolymerization of MA–VAc.

conversion from a prerun. As can be seen in Figure 9, good agreement is obtained between the densimetry-based and gravimetry-based conversion–time curve for this copolymerization of MA and VAc. From this it can be concluded that densimetry can be used as a qualitative method to obtain on-line conversion in emulsion copolymerizations if reactions are performed repeatedly. Note that at ca. 70% conversion all MA reacted as a consequence of composition drift. The increased polymerization rate at 70% conversion is a result of the different kinetic behavior of the homopolymerization of VAc.

The use of on-line GC to determine overall monomer ratios proved to be a valuable method to monitor composition drift. Comparison of on-line GC with off-line monomer ratio results ($q_{VAc/MA}$ = overall concentration of VAc/concentration of MA) shows good agreement as can be seen in Figure 10. For the monomer system MA–VAc a complete on-line GC analysis of the reaction mixture could
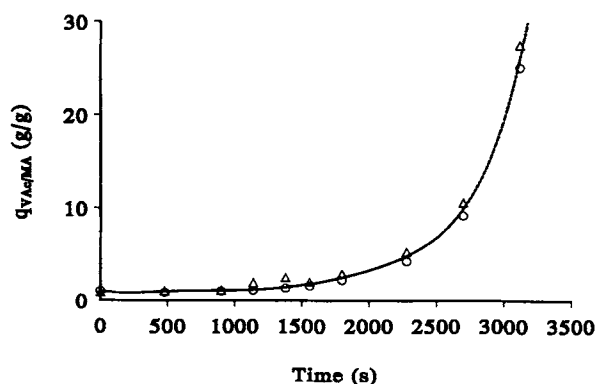

Figure 10   (○) On-line and (△) off-line monomer ratios determined from gas chromatography for the emulsion copolymerization of MA–VAc are depicted as a function of time together with a fit through both sets of data (line).
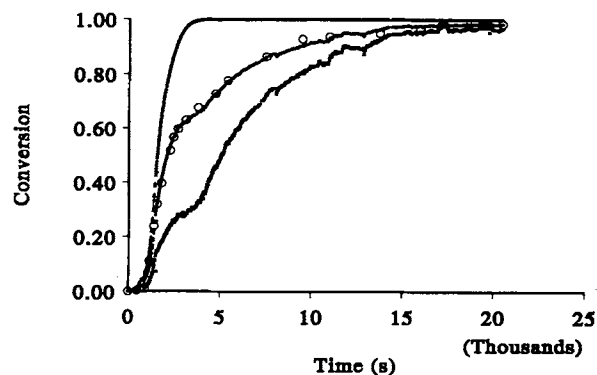
Figure 11   Partial and total conversion calculated from on-line densimetry and on-line gas chromatography are shown for methyl acrylate (top line) and vinyl acetate (bottom line) as a function of time. The overall conversion is calculated from on-line measurements (middle line) and gravimetry data (○).

be performed every 3 min. Although total conversion was completed only after approximately 9 h, a considerable composition drift led to complete conversion of MA within 1 h. Therefore, the number of samples was limited and no duplicate measurements could be taken. Fitting the monomer ratio–time data enables one to calculate the overall monomer ratio at any time during the copolymerization reaction.

Combining conversion–time values with overall monomer ratio–time values enables the calculation of the partial conversion of the separate monomers as a function of time (or conversion). For the calculation of the conversion of the MA and VAc separately, the following equations can be used:

$$x_{VAc,t} = 1 - \frac{(MA_o + VAc_o) \cdot (1 - x_{tot,t})}{VAc_o(1 + 1/q_{VAc/MA,t})} \quad (4a)$$

$$x_{MA,t} = 1 - \frac{(MA_o + VAc_o) \cdot (1 - x_{tot,t})}{MA_o(1 + q_{VAc/MA,t})} \quad (4b)$$

where: $x_{VAc,t}$, $x_{MA,t}$, and $x_{tot,t}$ represent the partial conversion of VAc, MA, and the total, overall weight conversion at time t, respectively; MA_o and VAc_o represent the initial mass of monomers MA and VAc at the beginning of the reaction; and $q_{VAc/MA,t}$ represents the overall monomer ratio of VAc over MA at time t. Combining on-line density measurements ($x_{tot,t}$) and on-line GC ($q_{VAc/MA,t}$) results in the partial conversions of the separate monomers as a function of time. This results in very detailed information about the partial conversion of the separate monomers MA and VAc in a batch emulsion copolymerization (recipe Table II) illustrated in Figure 11. Comparison of theoretical predictions[17] with exper-
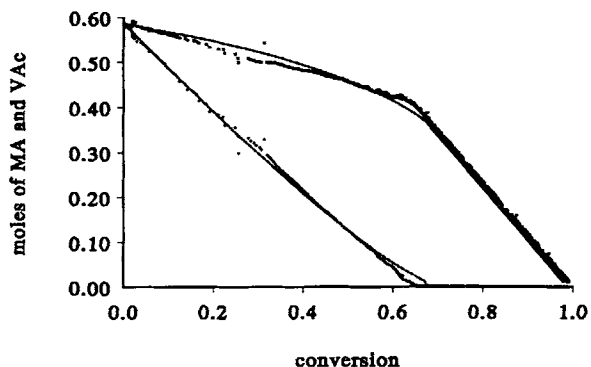
Figure 12 Experimentally determined absolute monomer amounts of methyl acrylate (bottom symbols) and vinyl acetate (top symbols) resulting from on-line densimetry and on-line gas chromatography are compared with theoretical predictions (methyl acrylate, bottom line; vinyl acetate, top line).

imental results for the copolymerization of MA and VAc shows excellent agreement seen in Figure 12 where the absolute numbers of moles of MA and VAc are depicted as a function of conversion.

CONCLUSIONS

For relatively water soluble monomers such as VAc and MA it has been shown that the specific volume of the monomers in the aqueous phase is different from the specific volume of the pure (monomer droplets) monomers leading to two linear regions in the specific volume–conversion curve of an emulsion homopolymerization. It was illustrated that for low solids reactions of VAc the volume additivity assumption is no longer valid. In these complicated situations conversion can be calculated from densimetry data either by assuming two linear regions for saturation and partial swelling and using the volume additivity assumption in the separate regions, or by calibrating the specific volume values with gravimetry values.

For the emulsion copolymerization of MA and VAc the combination of on-line densimetry with on-line GC proved to be a powerful method of determining the partial conversion of both monomers as a function of time. Comparison of the on-line data with off-line results and theoretical predictions gave satisfactory agreement. On-line densimetry can always be used as a qualitative method to obtain on-line conversion data for emulsion (co)polymerizations if reactions are performed repeatedly. It should be noted that the approach presented in this article, viz. the on-line determination of partial con-

versions of both monomers participating in the batch emulsion copolymerization reaction, can be used for any desired monomer pair.

REFERENCES

1. K. J. Abbey, *ACS Symp. Ser.*, **165**, 345 (1981).
2. F. J. Schork and W. H. Ray, *ACS Symp.*, **165**, 505 (1981).
3. C. H. M. Caris, R. P. M. Kuijpers, A. M. van Herk, and A. L. German, *Makromol. Chem., Macromol. Symp.*, **35/36**, 535 (1990).
4. A. Penlidis, J. F. MacGregor, and A. E. Hamielec, *Polym. Proc. Eng.*, **3**, 185 (1985).
5. D. C. H. Chien and A. Penlidis, *JMS-Rev. Macromol. Chem. Phys.*, **C30**, 1 (1990).
6. P. D. Gossen and J. F. MacGregor, *J. Colloid Interface Sci.*, **160**, 24 (1993).
7. S. Canegallo, G. Storti, M. Morbidelli, and S. Carrà, *J. Appl. Polym. Sci.*, **47**, 961 (1993).
8. E. M. Verdurmen, E. H. Dohmen, J. M. Verstegen, I. A. Maxwell, A. L. German, and R. G. Gilbert, *Macromolecules*, **26**, 268 (1993).
9. L. Rios, C. Pichot, and J. Guillot, *Makromol. Chem.*, **181**, 677 (1980).
10. G. H. J. van Doremaele, Ph.D. Thesis, Eindhoven University of Technology, The Netherlands, 1990.
11. M. Alonso, M. Alivers, L. Puigjaner, and F. Recasens, *Ind. Eng. Chem. Res.*, **26**, 65 (1987).
12. L. F. J. Noël, I. A. Maxwell, and A. L. German, *Macromolecules*, **26**, 2911 (1993).
13. O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Wiley, New York, 1972.
14. E. W. Washburn, C. J. West, N. E. Dorsey, F. R. Bichowsky, and A. Klemenc, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, McGraw-Hill, New York and London, 1928.
15. R. C. Weast, *CRC Handbook of Chemistry and Physics*, 66th ed., New York, 1985.
16. A. L. German and D. Heikens, *J. Polym. Sci., A1*, **9**, 2255 (1971).
17. L. F. J. Noël, J. M. A. M. van Zon, I. A. Maxwell, and A. L. German, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 1009 (1994).