

Determination of the maximum swellability of polymer for monomer using conductivity measurements

Citation for published version (APA):

Noel, E. F. J., Janssen, R. Q. F., van Well, W. J. M., Herk, van, A. M., & German, A. L. (1995). Determination of the maximum swellability of polymer for monomer using conductivity measurements. *Journal of Colloid and Interface Science*, 175(2), 461-469. <https://doi.org/10.1006/jcis.1995.1476>

DOI:

[10.1006/jcis.1995.1476](https://doi.org/10.1006/jcis.1995.1476)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Determination of the Maximum Swellability of Polymer by Monomer Using Conductivity Measurements

LILIAN F. J. NOËL, ROY Q. F. JANSSEN, WILLY J. M. VAN WELL, ALEX M. VAN HERK, AND ANTON L. GERMAN¹

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

Received November 28, 1994; accepted April 7, 1995

The maximum swellability of the polymer phase by monomer is an important parameter in emulsion polymerization. This parameter can be determined either by traditional monomer partitioning experiments or by conductivity measurements. The use of conductivity measurements to determine swellability values is new and rather simple. Compared to conventional monomer partitioning experiments it is less laborious and, in those cases where the monomer-saturated polymer phase has a higher density than the saturated aqueous phase, more accurate results can be obtained. For styrene (Sty) and methyl methacrylate (MMA), the maximum swellabilities were determined in a series of Sty–MMA copolymers by traditional monomer partitioning experiments and by conductivity measurements. From the good agreement it could be concluded that conductivity measurements indeed are a useful method of determining maximum swellability values. © 1995

Academic Press, Inc.

Key Words: emulsion polymerization; copolymerization; swellability; monomer partitioning; conductivity.

INTRODUCTION

Monomer partitioning between the polymer, monomer droplet, and aqueous phase is an important phenomenon in emulsion polymerization. The two most important parameters determining monomer partitioning are the water solubility and the maximum swellability of polymer by monomer (1–3). Determination of the latter parameter by monomer partitioning experiments is very laborious since it includes centrifugation of the emulsion and separation and analysis of the separate phases. In cases where the density of the monomer-saturated polymer phase (also known as the monomer-swollen polymer phase) is lower than that of the saturated aqueous phase, the monomer and polymer phase will both lie on top, making exclusive isolation of the polymer phase and accurate determination of the maximum swellability difficult. Recently, conductivity measurements have been introduced as a new on-line method to monitor

the course of emulsion polymerization reactions (4–6). The use of conductivity in emulsion polymerizations is quite new, and the promising technique can easily be extended to swellability determinations.

Conductivity measurements visualize the mobility of the ions in a mixture: the mobility of free surfactant molecules (high mobility) is different from the mobility of surfactant molecules incorporated in micelles or adsorbed at a (particle) surface (low mobility) (4). Since thermodynamic equilibrium can be assumed between free ions and ions adsorbed at a surface, the mobility, and therefore the conductivity, will change with the total particle surface. Furthermore, the critical micelle concentration (CMC) depends on the type and amount of both monomer and initiator (4, 7, 8). In intervals I and II in emulsion homopolymerization the conductivity will decrease with conversion mainly as a result of a growing total surface area. Note that the increase in surface area with conversion in intervals I and II is a direct result of the large difference in particle size and particle concentration between the large number of growing polymer particles and the smaller number of disappearing large monomer droplets. In interval III the concentration of surfactant molecules will generally be below the CMC. However, depending on the water solubility of the monomer, interval III can begin before interval I is ended. In these cases micelles can be present at the beginning of interval III. Both the CMC and the adsorption of surfactant on the particle surface will be influenced by the monomer concentration in the aqueous phase. In stage III the conductivity will increase either by an increase of the CMC or by desorption of surfactant molecules from the particle surface. This increase is normally supported by a decreasing total particle surface, which again leads to a redistribution of surfactant molecules until equilibrium is reached. Note that the total surface area will not decrease in case water-soluble monomers are used at low monomer-to-water ratios. As a result of the above-mentioned features, a minimum in conductivity will be found at the beginning of interval III in emulsion polymerization indicating the conversion where the monomer droplets have disappeared. Thus, from these data the maximum swellability can be determined.

The major advantage of conductivity measurements as

¹ To whom correspondence should be addressed.

compared with monomer partitioning experiments is that it is a less laborious method with comparable results and at least similar accuracy (accuracy is approximately 10%). As a result of the ultracentrifugation step used in the conventional monomer partitioning experiments, the monomer droplet, the aqueous, and the monomer-saturated polymer particle phases will be separated into three layers. Normally the monomer-saturated polymer phase is the bottom layer (highest density), the aqueous phase is the middle layer, and the monomer phase is the top layer. The polymer phase can easily be isolated and analyzed in these cases. However, in those cases where the monomer-saturated polymer phase has a lower density than the saturated aqueous phase, the monomer-saturated polymer phase and the monomer droplet phase will both lie on top, making exclusive isolation of the monomer-swollen polymer phase, without including any monomer from the monomer layer, extremely difficult. In these particular cases it is evident that better swellability values can be obtained by means of conductivity measurements. A further advantage of conductivity over conventional monomer partitioning experiments is the possibility to determine maximum swellabilities under reaction conditions, i.e., in the presence of, among others, initiator. It is obvious that the use of initiator in conventional monomer partitioning experiments needs to be avoided in order to prevent polymerization.

The swellabilities of methyl methacrylate (MMA) and styrene (Sty) in polystyrene, polymethyl methacrylate, and polystyrene-polymethyl methacrylate with varying copolymer compositions have been determined with conventional monomer partitioning experiments by several investigators (9–11). These swellabilities have been determined at several temperatures and copolymer compositions and will be discussed in detail together with the results of new monomer partitioning experiments under Results and Discussion. The results of conventional monomer partitioning experiments will be compared with on-line conductivity measurements of *ab initio* homopolymerizations of Sty and MMA (data of Janssen and co-workers (4, 6)) at 60 and 50°C (data of Fontenot and Schork (5)). Furthermore, a *seeded* emulsion copolymerization of Sty and MMA was monitored by off-line conductivity measurements. The advantage of a *seeded* reaction as compared with *ab initio* reactions is that the total surface area of the polymer particles is known as a function of conversion, if the particle size and particle concentrations of the seed latex are known. Based on these data the total surface area can be estimated and compared with conductivity data. Model predictions (3) of the *seeded* emulsion copolymerization were performed using maximum swellabilities that were determined by *ab initio* reactions. Comparison of experimental results of the *seeded* emulsion copolymerization with model predictions will show whether maximum

swellabilities have been obtained that are useful in practical situations.

EXPERIMENTAL

Materials

The following materials were used for the emulsion copolymerizations, for the monomer partitioning experiments, and for the determination of the density: reagent grade styrene (Janssen Chimica, Tilburg, The Netherlands), methyl methacrylate (Merck, Hohenbrunn, Germany), doubly distilled water, sodium persulfate (NaPS, p.a., Fluka AG, Buchs, Switzerland) as initiator, sodium dihexyl sulfosuccinate (Aerosol MA-80, Cyanamid, Rotterdam, The Netherlands), and sodium dodecyl sulfate (SDS, Fluka AG, Buchs, Switzerland) as surfactants and sodium carbonate (Na_2CO_3 , p.a., Merck, Darmstadt, Germany) as buffer. Before use in the emulsion polymerizations, the Sty and MMA were distilled under reduced pressure in order to remove inhibitor. The middle fraction was cut and stored at 4°C. In order to prevent polymerization during monomer partitioning experiments, MMA and Sty were applied as received without any further purification.

Emulsion Polymerization Reactions

In order to obtain latices for monomer partitioning experiments and densimetry purposes, emulsion (co)polymerizations were performed in a 1.3-liter stainless steel reactor fitted with four baffles at 90° intervals and a six-bladed turbine impeller stirred at 200 rpm. The recipes for these emulsion copolymerizations which were allowed to polymerize for at least 14 h at 65°C are given in Table 1. The main purpose of these emulsion copolymerizations was obtaining polystyrene-methyl methacrylate latices with varying copolymer composition. Before the seed latices were used in monomer partitioning experiments and densimetry, they were dialyzed in membrane tubes in order to remove excess surfactant, initiator, oligomers, buffer, and monomer. The dialysis water was changed every 2 h until the conductivity of the water surrounding the membrane tube remained constant in time at a value close to the value for distilled water. The solids content (determined by gravimetry), the copolymer composition in mole fraction of MMA (F_{MMA} , calculated from the initial monomer amounts, knowing that a conversion of 100% is reached), and the particle size (d_w , weight average particle diameter from sedimentation (DCP, Brookhaven Instruments Disk Centrifuge Photosedimentometer) and transmission electron microscopy (TEM, Jeol model JEM 2000 FX)) of the resulting latices are depicted in Table 2.

The reaction conditions and recipe of the on-line monitored *ab initio* batch emulsion polymerizations of Sty and

TABLE 1
Emulsion Copolymerization Recipes of Reactions Performed on Behalf of Monomer Partitioning Experiments

	Ingredients (g)				
	Latex 1	Latex 2	Latex 3	Latex 4	Latex 5
Sty	231.446	188.216	125.825	62.502	0
MMA	0	64.926	124.949	117.14	230.073
Water	699.50	758.56	739.61	772.07	697.91
MA-80	10.486	10.320	11.842	10.549	10.787
Na ₂ CO ₃	0.571	0.705	0.694	0.660	0.587
NaPS	0.697	0.761	0.757	0.715	0.705

MMA are given in detail elsewhere (4, 6). The initiator used in these reactions was the sodium salt of 4,4'-azo-bis-(4-cyanopentanoic acid).

Conventional Monomer Partitioning

Monomer partitioning experiments were performed for the monomer system Sty-MMA using the ultracentrifuge method (1, 2, 12). A latex with known solids content was mixed with known amounts of Sty or MMA at a temperature of 40°C in the absence of initiator. Equilibrium was reached within 24 h by shaking, followed by heating to 40°C at which temperature the solution was maintained for approximately 15 h. The different phases were separated using an ultracentrifuge (45,000 rpm Centrikon T-2060, 1–2 h) at 40°C. At saturation swelling the monomer concentrations in the particles were determined by means of gas chromatography after dissolving the monomer swollen polymer phase in tetrahydrofuran with toluene as internal standard. The GC analyses were performed utilising a Hewlett-Packard (HP) 5890A gas chromatograph, an HP 3393A integrator, an HP 7673A automatic sampler and a capillary HP-5 column (cross-linked 5% Ph Me silicone; 30 m × 0.53 mm × 2.65 μm). Determination of the dry solids content of the sample gave the polymer content which was needed to make corrections for the amount of aqueous phase present within the polymer phase. For the determination of the monomer con-

centration of MMA in the aqueous phase a saturated water-MMA mixture was thermostated at 40°C. After equilibrium was reached, phase separation was allowed to occur. The monomer concentration of MMA in the aqueous phase was determined by means of gas chromatography of a sample taken from the saturated aqueous phase using toluene as an internal standard. This mixture was stabilized by dilution with an acetone-water mixture.

Densimetry

Densimetry was performed using a thermostated Anton Paar DMA 10 density cell calibrated with water and toluene. In order to obtain accurate density values of copolymers all latices are diluted (to prevent coagulation) and degassed at the temperature at which the density determination is performed. The copolymer density can be calculated from the latex density and the solids content of the diluted latex using the equation (13)

$$1/\rho_l = x_p/\rho_p + x_s/\rho_s, \quad [1]$$

where x_p and x_s are the mass fractions of the polymer and serum (density of the aqueous phase) which can be calculated from the solids content, and ρ_l , ρ_p , and ρ_s represent the densities of the total latex system, the copolymer, and the serum, respectively.

Seeded Emulsion Copolymerization

The *seeded* emulsion copolymerization was performed in the same 1.3-liter stainless steel reactor as described above. The reactor was filled with monomers, water, seed latex, buffer, and surfactant (SDS) at room temperature (recipe in Table 3). The polymer phase was allowed to swell with monomer for at least 20 h. After being heated to 40°C the initiator was added to start the reaction. The reaction mixture was stirred at 300 rpm.

The reaction was monitored by gravimetry yielding conversion-time curves, by gas chromatography providing the overall monomer fractions as a function of time, and by

TABLE 2

Solids Content, Copolymer Composition in Mole Fraction of MMA (F_{MMA}) and Copolymer Density (at 40°C) of the Various Latices Prepared (See Table 1)

Latex number	Solids content (%)	F_{MMA}	d_w (nm)	Density (g/cm ³)
1	24.72	0	138	1.014
2	24.61	0.256	122	1.059
3	23.19	0.498	93	1.088
4	23.45	0.652	98	1.106
5	22.52	1	127	1.163

TABLE 3

Recipe of the Seeded Sty-MMA Reaction Performed at 40°C That Was Monitored by Conductivity, Gravimetry, and Gas Chromatography

Ingredients	Amounts (g)
Water	783.806
Sty	135.238
MMA	112.003
NaPS	0.742
NA ₂ CO ₃	0.627
SDS	0.651
Seed polymer	39.921

Note. Particle size and particle concentration of the seed latex were $d_p = 64$ nm (dynamic light scattering; Malvern Autosizer IIc 90° fixed angle at 25°C) and $N_c = 5.15 \times 10^{-17}$ particles/liter, respectively.

conductivity measurements resulting in conductivity as a function of time. The experimentally determined composition drift results were compared with theoretical predictions (3).

RESULTS AND DISCUSSION

Densimetry

Accurate density values of Sty and MMA monomer and copolymer are needed to allow calculation of polymer and monomer volumes; based on these values, maximum swellabilities were determined. The density of the copolymer latices were determined experimentally. The results, listed in Table 2, are depicted as a function of the mole fraction MMA in the copolymer in Fig. 1. From this it can be seen that the copolymer density is a linear function of the mole fraction MMA units. The experimentally determined densities of the monomers at 40°C were $\rho_{\text{MMA}} = 0.918$ g/cm³ and $\rho_{\text{Sty}} = 0.887$ g/cm³. Both values agree very well with

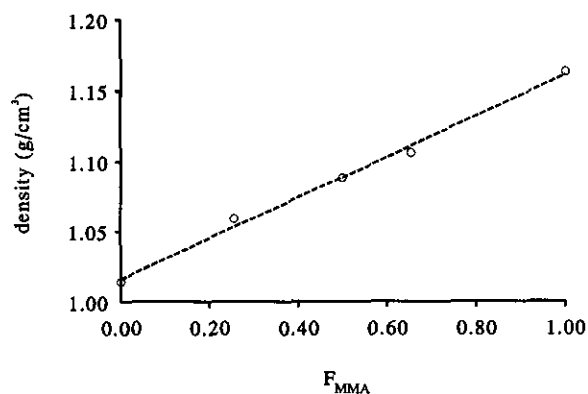


FIG. 1. Experimentally determined copolymer density as a function of the mole fraction of MMA in the copolymers.

TABLE 4

Monomer (Sty, MMA) and Polymer Density (pMMA, pSty) Values at 40, 50, and 60°C Used to Calculate Maximum Swellabilities of MMA and Sty

	Density (g/cm ³)		
	40°C	50°C	60°C
Sty	0.887		0.869
MMA	0.918	0.914	0.909
pMMA	1.179	1.174	1.169
pSty	1.046		1.040

Note. Some of these data were determined experimentally and some were obtained from extrapolation or interpolation of literature values (14, 15).

(extrapolated) literature values (14, 15). The density values used to calculate the maximum swellabilities for the Sty and MMA homopolymerizations at various temperatures are listed in Table 4.

Monomer Partitioning Results

Nomura *et al.* (9) found that the maximum swellabilities of Sty and MMA in the copolymer Sty-MMA were independent of the copolymer composition resulting in the following range of values at 50°C: $[\text{Sty}]_{\text{p,sat}} = 5.2\text{--}5.8$ mol/liter and $[\text{MMA}]_{\text{p,sat}} = 6.3\text{--}6.9$ mol/liter. In the first place these results were compared with results of Aerds *et al.* (10), who determined the swellability of Sty and MMA at room temperature in Sty-MMA latices with copolymer compositions of $F_{\text{MMA}} = 0.25$ and 0.5. In order to study the effects of copolymer composition on the swellability of monomer in copolymer, during the present investigation monomer partitioning experiments were performed at 40°C for both Sty and MMA in Sty-MMA latices with different copolymer compositions. It has been shown before (1) that the dependency of the maximum swellability on the particle size is within experimental error for particles with diameters as large as used in this investigation (see Table 2). Accurate maximum swellability values of MMA at 40°C as a function of copolymer composition could be determined experimentally and are depicted in Fig. 2 together with other literature values (the values of Nomura *et al.* (9) were estimated to be constant (16) $[\text{MMA}]_{\text{p,sat}} = 6.3$ mol/liter).

The determination of the swellability by styrene in the different copolymers was rather hard to perform accurately since the density of the monomer-swollen polymer phase was lower than the density of the aqueous phase. As a result the monomer droplet phase and the saturated polymer phase are both on top, making accurate sampling complicated. Other investigators may have experienced similar problems when determining the swellability by Sty as can be seen from the large differences among swellability values depicted in

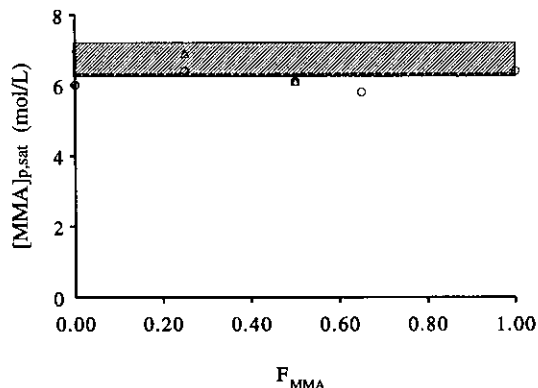


FIG. 2. Comparison of maximum swellability values of MMA in the polymer phase as a function of copolymer composition. Data of Nomura *et al.* (9) at 50°C (box), Aerdtts *et al.* (10) at room temperature (Δ), and the present work at 40°C (\circ). The dashed line represents the average value of 6.3 mol/liter.

Fig. 3. Assuming volume additivity of monomer and polymer in the monomer-swollen polymer phase the *minimum* swellability of Sty in the various copolymers can be calculated setting the density of the monomer-swollen polymer phase equal to the density of water in case the densities of water, monomer, and copolymer are known. These minimum swellability values are compared in Fig. 3 with results of Nomura *et al.* (9) (estimated to be constant at $[\text{Sty}]_{p,\text{sat}} = 5.5$ mol/liter) and Aerdtts *et al.* (10) and with the swellability value of Sty in polystyrene at 45°C ($[\text{Sty}]_{p,\text{sat}} = 6.5$ mol/liter) that was determined by van Doremale *et al.* (11). From the MMA results it can be concluded that temperature (from 20 to 50°C) and copolymer composition effects upon the maximum swellability of MMA in polystyrene, polymethyl methacrylate, and polystyrene-polymethyl methac-

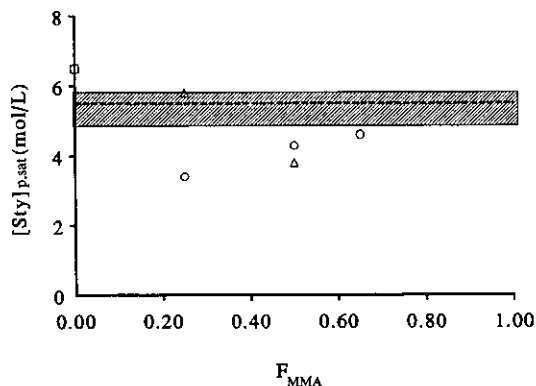


FIG. 3. Comparison of maximum swellability values of Sty in the polymer phase as a function of copolymer composition. Data of Nomura *et al.* (9) at 50°C (box), Aerdtts *et al.* (10) at room temperature (Δ), and van Doremale *et al.* (11) at 45°C (\square). In the present work only a minimum swellability value of Sty in the copolymer could be determined at 40°C (\circ). The dashed line represents the average value of 5.5 mol/liter.

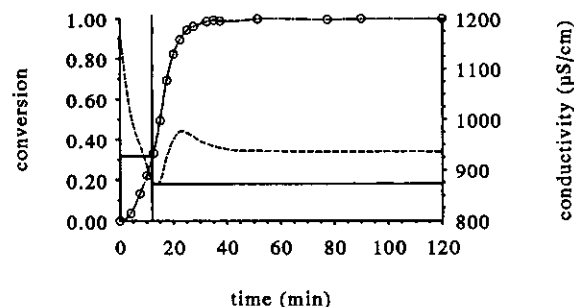


FIG. 4. Conversion (\circ) and conductivity (---) as a function of time for an *ab initio* MMA emulsion polymerization reaction. The vertical line represents the II-III transition.

rylate can be neglected. Analogous to the MMA results we assume that the swellability of Sty-MMA copolymers with Sty is independent of temperature in the range from 20 to 50°C. Based on this important result we also assume the swellability of Sty-MMA copolymers with Sty to be temperature independent. As a result of this we can conclude that the Sty-MMA copolymer independent swellability results for Sty found by Nomura *et al.* (9) are correct, leading to swellability values that are independent of the copolymer composition. Based on the above considerations the following swellability results for MMA and Sty are assumed to be the best ones: $[\text{MMA}]_{p,\text{sat}} = 6.3$ mol/liter and $[\text{Sty}]_{p,\text{sat}} = 5.5$ mol/liter.

Note, however, that although the maximum swellability results of MMA-Sty are approximately independent of the copolymer composition, this certainly does not have to be a result of general validity.

Conductivity Measurements

Ab initio Reactions

On-line conductivity measurements performed by Janssen *et al.* (4) and by Fontenot and Schork (5) proved to give detailed information about emulsion polymerizations. It was shown that the conductivity reaches a minimum value at the interval II-III transition. This is illustrated by two typical conductivity-time and conversion-time curves (Figs. 4 and 5) of Sty and MMA (data from Janssen and co-workers (4, 6)). As shown by Janssen (6), the behavior of the conductivity signal can be explained taking into account that, as a first approximation, the conductivity is the sum of three separate contributions: (i) the (free) surfactant concentration in the aqueous phase, (ii) the CMC of surfactant in water, and (iii) the initiator concentration.

Surfactant Concentration and CMC

Initially in an emulsion system the surfactant will be present partly dissolved in the aqueous phase and partly in the

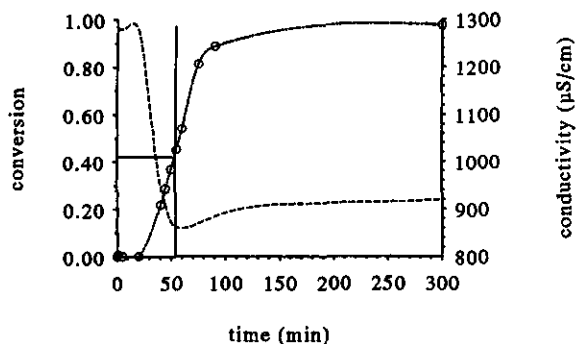


FIG. 5. Conversion (○) and conductivity (---) as a function of time for an *ab initio* Sty emulsion polymerization reaction. The vertical line represents the II–III transition.

form of micelles if the CMC is exceeded. In the particle growth period, i.e., in intervals I and II, the surface area is strongly increased to an extent that depends on the density difference between monomer and polymer, temperature, swellability, particle size, and number. In this particle growth period, surfactant molecules will migrate toward the particle surface where their mobility is much lower. As a result, the conductivity will decrease. As soon as the monomer droplets have disappeared at the beginning of interval III, the monomer concentration in both the aqueous phase and the polymer particle phase will decrease with conversion, thus affecting the CMC and the total surface area.

CMC. It has been shown in the literature that the critical micelle concentration depends on the type and amount of both the monomer and initiator (4, 7, 8). The presence of monomers will lead to a considerable decrease in the CMC value. During interval III of a reaction the monomer concentration in the aqueous phase will decrease, leading to an increasing CMC. Since the monomer concentration in the aqueous phase influences the partitioning of surfactant molecules between the aqueous phase and the particle surface, some surfactant molecules will be released into the aqueous phase, thus increasing the conductivity. This phenomenon will occur even in interval III, where no more micelles are present.

Total surface area. In interval III of an emulsion polymerization the total surface area will decrease unless secondary nucleation occurs or if the monomer is so water soluble that the amount of monomer that is continuously extracted from the aqueous phase during interval III still results in growth, as can be the case for MMA at low monomer-to-water ratios (6). This means that, as a result of changing CMC and total surface area with conversion, a redistribution of surfactant occurs, leading to an increase in conductivity. To what extent the surfactant is released and conductivity is increased depends on the surface coverage of the polymer with SDS ($0.5 \text{ nm}^2/\text{SDS molecule}$ for polystyrene and 0.79

$\text{nm}^2/\text{SDS molecule}$ for polymethyl methacrylate (17) and the critical surface coverage, i.e., the minimum number of SDS molecules per particle needed for stabilization. The presence of surface-active oligomers probably plays an important role in this, although it is not yet clear to what extent.

Initiator Concentration

The half-life time of initiator is temperature and reaction condition dependent (18). For the initiator 4,4'-azo-bis-(4-cyanopentanoic acid) at 60°C in pure water the half-life time is 39 h. This value for the half-life time may decrease orders of magnitudes on the addition of monomer (18). Based on a maximum half-life time of 39 h it can be estimated that during interval III (2 to 3 h), a few percent of the total initiator amount will dissociate leading to a slight increase in the conductivity (dissociation leads to the formation of two ionic radicals, each of which is more mobile than the original molecule). However, as a result of polymerization these ion radicals will quickly add monomer, leading to a decrease in conductivity. Note that the exact effect on conductivity is still not totally clear and probably depends on the monomer–initiator combination.

The exact nature of all factors determining the conductivity signal has not yet been fully elucidated and is still under investigation (6). Nevertheless, when one accounts for the above-mentioned effects, the following can be concluded:

1. In intervals I and II the polymer particles will grow at the expense of the monomer droplets. In these intervals the strong increase in the total surface area will probably be the largest factor determining the conductivity; the surfactant will migrate toward the growing particle surface where its mobility is lower than in the aqueous phase, leading to a strong decrease in conductivity (4). The contribution to the conductivity of the dissociating initiator will be relatively small in intervals I and II because of the low dissociation rate. As a result of the constant monomer concentration in the aqueous phase and the nearly constant initiator concentration in intervals I and II, the CMC is assumed to be constant.

2. In interval III the particles have stopped growing. Therefore, only conductivity increasing effects remain. They are the release of surfactant from the particles as a result of an increase in CMC, a decrease in surface area, and the dissociation of the initiator. Both the increase in CMC and the growth of the particles will be more pronounced in the case of MMA than in that of Sty (4, 6).

As discussed above, the conductivity is a sum of a series of contributions that will influence one another. At the end of interval II and in interval III these separate contri-

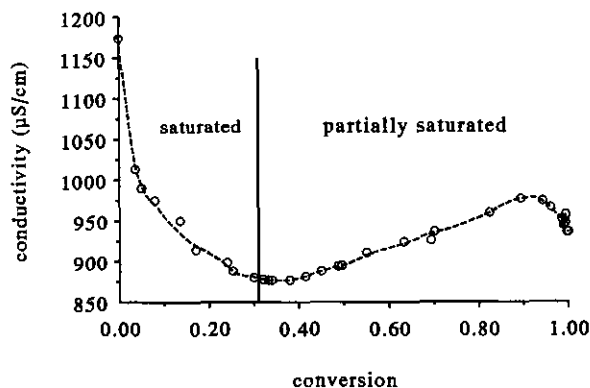


FIG. 6. Conductivity as a function of conversion for an *ab initio* MMA emulsion polymerization reaction (4).

butions may even cancel. Therefore, it is safe to say that the transition from interval II to III takes place at the end of the strong decrease in the conductivity. The fact that the minimum in the case of MMA is much more pronounced than in the case of Sty can be related to the difference in water solubility of the monomers. This probably leads to significant formation of oligomers in the aqueous phase contributing to the observed stronger increase in conductivity in interval III in the case of MMA as compared with Sty. In fact for MMA one can say that interval III is entered before interval I is ended, which means that micelles can still be present in interval III. It was mentioned earlier that the amount of monomer dissolved in the aqueous phase has a large impact on both the CMC and the conductivity (4). Combining the conversion and conductivity data shown in Figs. 4 and 5 results in the conductivity-conversion data depicted in Figs. 6 (MMA) and 7 (Sty). From these figures, the maximum swellability could be calculated at the conversions indicated by the vertical lines using the relationship

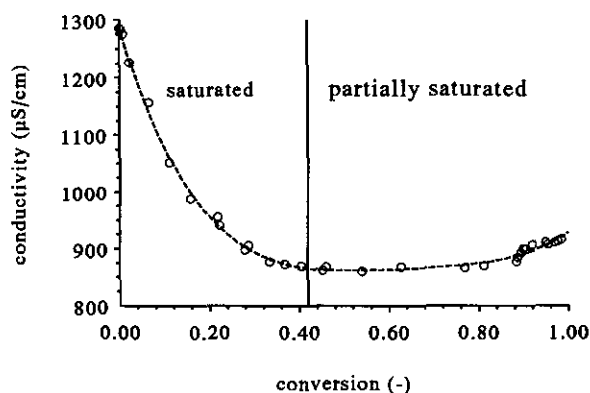


FIG. 7. Conductivity as a function of conversion for a *ab initio* Sty emulsion polymerization reaction (6).

TABLE 5

Conversions at the Interval II-III Transition as Determined from Conductivity Measurements, Temperature (T), and Amounts of Monomer and Water Used in the *ab initio* Batch Reactions of Fontenot and Schork (5) and Janssen and co-workers (4, 6)

	Janssen <i>et al.</i> (4)	Janssen (6)	Fontenot and Schork
II-III (%)	31	42	30
T (°C)	60	60	50
MMA (g)	42.59		220
Sty (g)		43.22	
Water (g)	900	900	510

maximum swellability

$$= \frac{\text{moles of monomer}}{\text{monomer volume} + \text{polymer volume}}, \quad [2]$$

where "moles of monomer" and "monomer volume" refer to the monomer in the polymer phase. The amount of monomer and polymer can be calculated from the II-III transition (Table 5), taking into account the water solubility of MMA (as determined from monomer partitioning experiments: ca. 0.12 mol/liter). From these data the number of moles of monomer in the aqueous and polymer phase as well as the monomer and polymer volumes can be calculated using the density values listed in Table 4. The maximum swellabilities resulting from these conductivity measurements are

$$\begin{aligned} \text{Maximum swellability by MMA at } 60^\circ\text{C: } [\text{MMA}]_{p,\text{sat}} \\ = 5.9 \pm 0.6 \text{ mol/liter} \end{aligned}$$

$$\begin{aligned} \text{Maximum swellability by Sty at } 60^\circ\text{C: } [\text{Sty}]_{p,\text{sat}} \\ = 5.2 \pm 0.5 \text{ mol/liter.} \end{aligned}$$

It should be noted that the deviation in the maximum swellability values is mostly determined by the selection of the correct conversion value for the II-III transition. Possible inaccuracies (maximum of 2%) in the density values result in deviations of 0.2 mol/liter at most.

From the MMA data at 50°C of Fontenot and Schork (5) listed in Table 5 the following maximum swellability value could be determined:

$$\begin{aligned} \text{Maximum swellability of MMA at } 50^\circ\text{C: } [\text{MMA}]_{p,\text{sat}} \\ = 6.8 \pm 0.7 \text{ mol/liter.} \end{aligned}$$

Comparison between the monomer partitioning and conductivity results shows acceptable agreement, as can be seen in Table 6. From this agreement it can be concluded that the effect of the presence of surfactant, buffer, and initiator on

TABLE 6

Maximum Swellability Values Resulting from Monomer Partitioning Experiments (50°C) and Conductivity Measurements (50 and 60°C)

	Monomer partitioning	Conductivity
Sty (mol/liter)	5.5	5.2 ± 0.5 (6)
MMA (mol/liter)	6.3	5.9 ± 0.6 (4); 6.8 ± 0.7 (5)

the maximum swellability in the present emulsion copolymerizations is within experimental error.

Seeded Reaction

For a seeded copolymerization of MMA with Sty (recipe in Table 3) the conductivity was measured off-line as a function of conversion because the reactor in which the seeded reaction was performed was not equipped with a port for on-line conductivity measurements. Model predictions were performed using the reactivity ratios of $r_{\text{MMA}} = 0.460$ and $r_{\text{Sty}} = 0.523$ (19) the water solubilities of $[\text{MMA}]_{\text{a,sat}} = 0.12$ mol/liter and $[\text{Sty}]_{\text{a,sat}} = 0.0038$ mol/liter, the maximum swellabilities of $[\text{MMA}]_{\text{p,sat}} = 5.9$ mol/liter and $[\text{Sty}]_{\text{p,sat}} = 5.2$ mol/liter, and the amount of seed polymer (Table 3). Note that the course of composition drift in emulsion copolymerization mainly depends on the reactivity ratios and the water solubilities. The maximum swellability affects only the conversion at which the monomer droplets disappear. The experimental conditions were selected in such a way that minimum composition drift is obtained. In Fig. 8 the predicted overall monomer mole fraction as a function of conversion is compared with experimental results, showing good agreement (Fig. 8) (3). The experimentally deter-

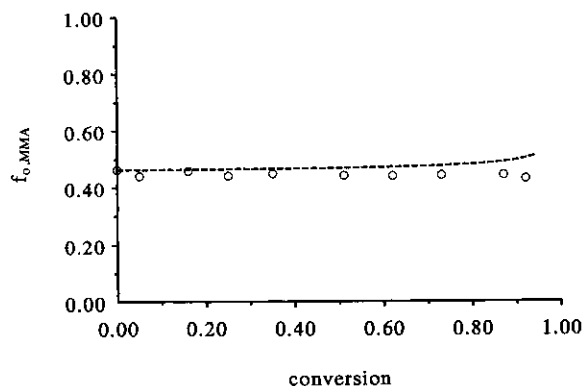


FIG. 8. Comparison of experimentally measured (○) and theoretically predicted (---) overall MMA mole fractions as a function of conversion. The model parameters used were $r_{\text{MMA}} = 0.460$, $r_{\text{Sty}} = 0.523$, $[\text{MMA}]_{\text{a,sat}} = 0.12$ mol/liter, $[\text{Sty}]_{\text{a,sat}} = 0.0038$ mol/liter, $[\text{MMA}]_{\text{p,sat}} = 5.9$ mol/liter, and $[\text{Sty}]_{\text{p,sat}} = 5.2$ mol/liter.

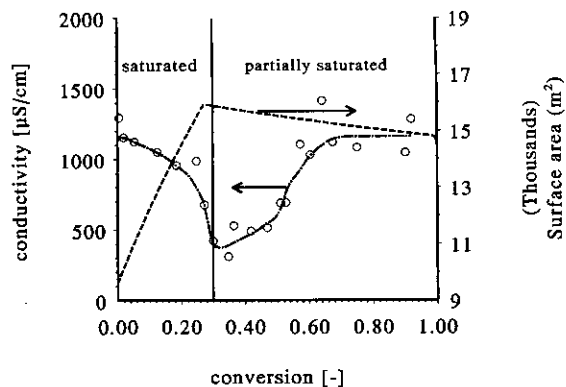


FIG. 9. Conductivity (experimental data, ○; fit, ---) and total surface area calculated from simplified model predictions (---) as a function of conversion for a seeded MMA–Sty copolymerization reaction. The vertical line represents the II–III transition that was predicted using maximum swellabilities as determined by conductivity measurements.

mined conductivity is given as a function of conversion in Fig. 9. The minimum in conductivity representing the II–III transition is illustrated with the vertical line at 30% conversion. Model predictions using the maximum swellabilities of $[\text{MMA}]_{\text{p,sat}} = 6.3$ mol/liter and $[\text{Sty}]_{\text{p,sat}} = 5.5$ mol/liter determined by conventional monomer partitioning experiments result in a predicted II–III transition at 28% conversion. However, using the maximum swellabilities of $[\text{MMA}]_{\text{p,sat}} = 5.9$ mol/liter and $[\text{Sty}]_{\text{p,sat}} = 5.2$ mol/liter determined by conductivity measurements, the II–III transition is predicted to be at 30% conversion. The conductivity minimum agrees better with the II–III transition predicted using the maximum swellabilities determined by conductivity measurements (vertical line at 30% conversion in Fig. 9) than with the prediction based on conventional monomer partitioning experiments (II–III transition at 28% conversion). From this result it can be concluded that both sets of maximum swellabilities of MMA and Sty used in the model prediction give good agreement between theory and experiment. *It is clear that the determination of maximum swellabilities using conductivity measurements results in accurate and trustworthy values.* In order to illustrate the changing total surface as a function of conversion, the sum of the swollen polymer particle surface and the monomer droplet surface was calculated based on the model prediction assuming a monomer droplet diameter of $1 \mu\text{m}$ and using the particle size (at 25°C: $d_c = 64$ nm) and particle concentration ($N_c = 5.15 \times 10^{17}$ particles/liter) of the seed latex. From Fig. 9 it can be seen that the total surface indeed increases strongly during interval II while there is only a minor decrease during interval III.

CONCLUSIONS

The maximum swellability of polymer by monomer can be determined by traditional monomer partitioning experi-

ments and by conductivity measurements. The use of conductivity measurements to determine swellability values is new and rather simple. Conductivity measurements are less laborious as compared with monomer partitioning experiments. Furthermore, more accurate results can be obtained, in particular, in cases like Sty at 40°C, where the polymer phase has a higher density than the saturated aqueous phase. The maximum swellabilities of styrene and methyl methacrylate were determined at various temperatures and for different styrene–methyl methacrylate copolymers by traditional monomer partitioning experiments, resulting in the values of $[MMA]_{p,sat} = 6.3$ mol/liter and $[Sty]_{p,sat} = 5.5$ mol/liter, independent of temperature (over the range 20–50°C) and Sty–MMA copolymer composition. The maximum swellability values as determined at 50 and 60°C by conductivity measurements, ($[MMA]_{p,sat} = 5.9$ mol/liter and $[Sty]_{p,sat} = 5.2$ mol/liter) agreed rather well with these monomer partitioning results. The conductivity data were found to give very reliable results, leading to the conclusion that conductivity measurements indeed are a useful and practical method of determining the maximum swellability.

REFERENCES

1. Maxwell, I. A., Kurja, J., van Doremale, G. H. J., and German, A. L., *Makromol. Chem.* **193**, 2065 (1992).
2. Noël, L. F. J., Maxwell, I. A., and German, A. L., *Macromolecules* **26**, 2911 (1993).
3. Noël, L. F. J., van Zon, J. M. A. M., Maxwell, I. M., and German, A. L., submitted for publication.
4. R. Q. F. Janssen, A. M. van Herk, and A. L. German, *Surf. Coat. Int. (JOCCA)* **76**(11), 455 (1993).
5. Fontenot, K., and Schork, F. J., *J. Appl. Polym. Sci.* **49**, 633 (1993).
6. Janssen, R. Q. F., thesis, Eindhoven, (1995).
7. Rosen, M. J., "Surfactants and Interfacial Phenomena." Wiley, New York, 1978.
8. Elworthy, P. H., Florence, A. T., and MacFarlane, C. B., "Solubilisation by Surface Active Agents." Chapman & Hall, London, 1968.
9. Nomura, M., Yamamoto, K., Horie, I., Fujita, K., and Harada, M., *J. Appl. Polym. Sci.* **27**, 2483 (1982).
10. Aerdt, A. M., Boei, M. M. W. A., and German, A. L., *Polymer* **34**, 574 (1993).
11. van Doremale, G. H. J., Geerts, F. H. J. M., Schoonbrood, H. A. S., Kurja, J., and German, A. L., *Polymer* **33**, 1914 (1992).
12. Maxwell, I. A., Kurja, J., van Doremale, G. H. J., German, A. L., and Morrison, B. R., *Makromol. Chem.* **193**, 2049 (1992).
13. Schork, F. J., and Ray, W. H., *ACS Symp.* **165**, 505 (1981).
14. Bandrup, J., and Immergut, E. H., "Polymer Handbook," 3rd ed. Wiley, New York, 1989.
15. Patnode, W., and Schreiber, W. J., *J. Am. Chem. Soc.* **61**, 3449 (1939).
16. Noël, L. F. J., Maxwell, I. A., van Well, W. J. M., and German, A. L., in preparation.
17. Vijayendran, B. R., *J. Appl. Polym. Sci.* **23**, 733 (1979).
18. Sarkar, S., Adkikari, M. S., Banerjee, M., and Konar, R. S., *J. Appl. Polym. Sci.* **35**, 1441 (1988).
19. Fukuda, T., Ma, Y., and Inagaki, H., *Macromolecules* **18**, 17 (1985).