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SHORT COMMUNICATION

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On-line surface tension measurements inside stirred reactors

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Abstract A method as well as an experimental set-up are described allowing on-line surface tension measurements directly inside stirred reactors at any temperature. The method is based on the finding that the difference between the maximum and the minimum pressure during bubble formation correlates strongly with the surface tension of the surrounding solution. Examples of applications are given concerning the discrimination of different surfactant solutions, the formation of surface-active compounds during chemical reactions, and emulsion polymerizations.

Key words Surface tension · Bubble pressure difference · Emulsion polymerization · Particle nucleation · Radical entry

Introduction

Surface tension measurements play an important role in colloid chemistry. In particular, on-line surface tension measurements inside stirred reactors – directly during a reaction – are of great interest. These measurements promise on-line information and hence control of reactions with participation of surface-active compounds which are not obtainable with other methods. Examples are heterophase polymerizations, surfactant synthesis, and monitoring of surfactant consumption. Different methods are known for measuring the surface tension of solutions, for instance [1–5], capillary rise, Wilhelmy plate, Du Nouy ring, shape of sessile or pendant drops, number of drops of liquid per unit time coming from an orifice of known size, and maximum pressure of a gas bubble; however, only the latter method is suited for quasi on-line measurements. In a series of papers Schork and Ray [6–9] reported the use of the maximum bubble pressure method to record the change in the surface tension during emulsion polymerization by by-passing the reaction mixture through a bubble tensiometer Chen and Penlidis [10] employed a similar type of tensiometer to measure the surface tension in the case of the continuous emulsion polymerization of vinyl acetate. The tensiometer was placed at the outlet of the last reactor of the series. Both techniques, the by-pass measurement and the measurement at the end of a series of reactors, have some drawbacks compared to an in situ measurement which can be carried out independently in each reactor of a series and hence is more advisable. The possibility of the on-line measurement of surface tension inside a reactor during emulsion polymerization is of special benefit as direct control of the level of free surfactant is possible.

The aim of this contribution is to report – to the best of our knowledge for the first time – an on-line method of surface tension measurement during a reaction directly inside a stirred reactor. It is a modification of the maximum bubble pressure method such that the pressure difference between bubble formation (maximum pressure) and bubble rip off (minimum pressure) is monitored. This makes the technique much more robust compared with the maximum pressure method. The technique is tested in several examples of surfactant dissolution, formation of a surface-active compound, surfactant-free emulsion polymerization, and emulsion polymerization in the presence of surfactants.

Experimental

The on-line bubble tensiometer

The centerpiece of the on-line bubble tensiometer is a differential pressure sensor (SENSORTECHNICS, SenSym SX01) with a scale range between −1 and +1 psi (±6.8947 kPa) which is able to measure from two sides. The positive side of the pressure sensor is connected with the capillary through which nitrogen continuously flows and generates the bubbles. The nitrogen was supplied by a double-stage high-pressure cylinder regulator (FMD 230-3; 0.1, Linde) to maintain a constant gas flux over the whole duration of the experiments. The negative side of the pressure sensor is connected with the reference capillary, which compensates the atmospheric as well as the hydrostatic pressure. A detailed description of the electronic parts can be found elsewhere [11].

Chemicals

Styrene, methyl methacrylate (MMA), sodium hydrogen carbonate, potassium peroxodisulfate (KPS), sodium lauryl sulfate (SDS), 1-octanol, and potassium permanganate (all from Sigma–Aldrich), Igepal CO880 (Rhone Poulenc), E30 (Leuna Werke), an alkyl sulfonate with an average carbon chain length of 15, ECD2930 (Akcros Chemicals), a C_{12} alcohol hemiester of maleic acid, SE1030 (Th. Goldschmidt), a block copolymer surfactant consisting of a styrene block with a molecular weight of 1000 g mol^{-1} and an ethylene oxide block with a molecular weight of 3000 g mol^{-1} and nitrogen 5.0 (Linde) were used as received except for the monomers which were treated as described below.

Deionized water was taken from a REWA ion-exchange water supply system. The monomers were distilled under reduced pressure to remove inhibitors and stored in a refrigerator. Prior to use, to check whether or not oligomers had been formed, a drop of monomer was added to an excess of methanol. Only oligomer-free monomers were used.

Reactor construction

All investigations were carried out batchwise in a 250-ml all-glass reactor with a heating jacket to control the temperature. The reactor was equipped with a paddle agitator, a reflux condenser, and a specially constructed bubble generator consisting of two identical capillaries, where one capillary serves to form the bubbles and simultaneously acts as a nitrogen inlet, and contains a valve on the bottom to remove the latex. Capillaries with diameters of 0.91, 0.45, and 0.25 mm were used. A schematic drawing of the whole device is shown in Fig. 1. It is stressed that the particular construction of the protecting cap of the bubble generator is only one possibility. It is not optimized and, hence, it is very likely that in future more effective constructions will be found.

The experiments were carried out as follows. Water (250 g) was brought into the reactor and allowed to equilibrate under stirring while the surface tension was monitored on-line. The stirring speed was adjusted to 120 rpm. After the surface tension had reached a constant value the experiments were started.

All polymerizations were carried out in such a way that after allowing the water to equilibrate at 70 °C, 3 g monomer was added. The reaction mixture was then allowed to reach the distribution equilibrium between the free monomer and water. The stirring was so gentle (120 rpm) that a free-monomer phase was formed on top of the water. After at least 30 min the surface tension again reached a constant value and hence the system was at equilibrium. The initiator (0.4 g KPS) was then added to start the reaction. The surface tension was monitored during the entire reaction.

Results

The bubble pressure difference (BPD) method

A bubble tensiometer is based on the capillarity phenomenon and hence the fundamental relation is the Young and Laplace equation [12]. The method works in such a way that the pressure is monitored while a flux of an inert gas is slowly blown through a capillary into a liquid. The development of the pressure during bubble formation and rip off is shown in Fig. 2. The pressure balance is given by Eq. (1), where P_S is the gas pressure necessary for gas bubbles to escape, P_A is the atmospheric pressure, P_H is the hydrostatic pressure, γ is the

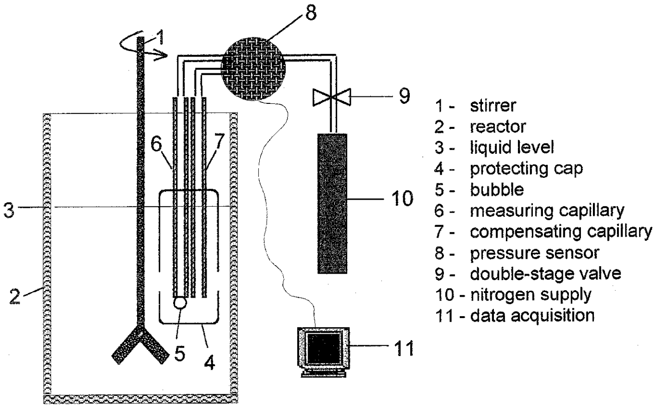

Fig. 1 Schematic drawing of the experimental set-up

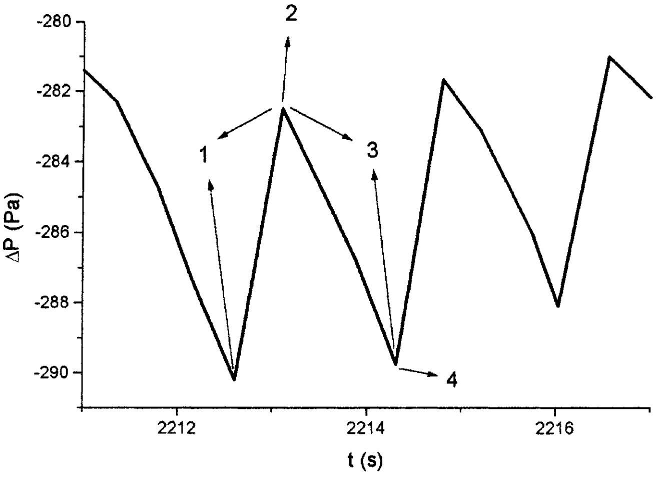

Fig. 2 Pressure change during bubble formation for water at 70 °C. Interval *1*: pressure inside the capillary rises and build up of the hemisphere; point *2*: hemisphere; interval *3*: hemisphere grows; point *4*: bubble rips off

surface tension of the liquid, R is the capillary radius, and ΣX_i denotes all other influences suppressing or promoting the escape of bubbles. An example of such an influence is the pressure induced by stirring. The term $2\gamma/R$ comes from the Young and Laplace equation and can be considered as the surface-tension pressure of the liquid.

$$P_S = P_A + P_H + \frac{2\gamma}{R} + \Sigma X_i \ . \tag{1}$$

In the case of the well-known maximum bubble pressure method [3, 8, 9] it is necessary to measure the maximum gas pressure in the capillary such that bubbles are quasi in an equilibrium situation and hence maintain their minimum size. This means that a bubble sits at the capillary edge to the liquid as a hemisphere with a radius that is equal to the radius of the capillary and does not grow. In this situation the bubble has its smallest size and hence the pressure will be highest. To maintain this situation without adjusting the gas pressure, which was tuned before to a value that allows a bubble flux through the capillary, is almost impossible. The bubble will unavoidably grow and hence the pressure will decrease until the bubble breaks away. Therefore, it is much easier to get accurate measurements if the hydrostatic pressure over the capillary projecting into the liquid is adjusted [3]; however, this method is unsuitable for online measurements directly inside stirred reactors. During bubble formation and break away the pressure changes in a very regular manner as illustrated by the example given in Fig. 2. Additionally, these data confirm the difficulties in measuring the maximum bubble pressure exactly.

In the Young and Laplace equation ($\Delta P_{\max} = 2\gamma/R$) ΔP stands for the difference between the maximum bubble pressure and the hydrostatic pressure when the corresponding experiments are carried out in the absence of disturbances, for instance, shear forces. Additionally, this relation is only valid if the bubbles possess an exactly spherical shape and if the ratio between R/a is as small as 0.05 [12], where a is the capillary constant defined by Eq. (2).

$$a^2 = \frac{2\gamma}{\Delta\rho \cdot g} \ . \tag{2}$$

$\Delta\rho$ is the density difference between the liquid and the gas phase and g is the acceleration due to gravity. The latter condition is almost fulfilled with a capillary diameter of 0.225 mm, however, due to the experimental conditions the escaping bubbles are not exactly spherical. Furthermore, the pressure does not go back to zero after a bubble has left the capillary (cf. Fig. 2). This was also observed by Razouk and Walmsley [13] in their differential maximum bubble pressure experiments using two capillaries with different radii and a pressure transducer. The data in Fig. 2 were obtained with the experimental set-up depicted in Fig. 1. The two capillaries are identical in size and depth of immersion. One capillary is used for bubble formation and the other is for compensating atmospheric as well as hydrostatic pressure and all other influences (first and foremost the stirrer speed).

Deviating from earlier results [8, 10], it turned out that the difference between the maximum pressure (hemisphere formation) and the minimum pressure (bubble escape) (δP) varies in a systematic way with the surface tension of the solution, but is independent of the depth of immersion of the capillary (cf. Figs. 3, 4) [11]. The surface tensions of the test solutions were varied by using acetone/water mixtures with different compositions (cf. Fig. 3). The correlation between δP

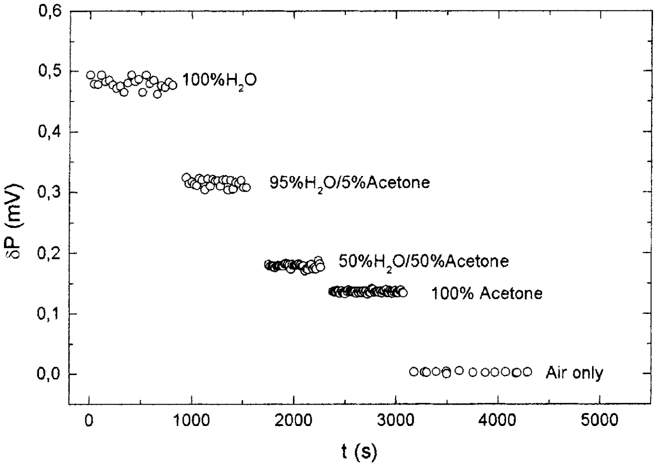

Fig. 3 Change in the bubble pressure difference for water/acetone mixtures

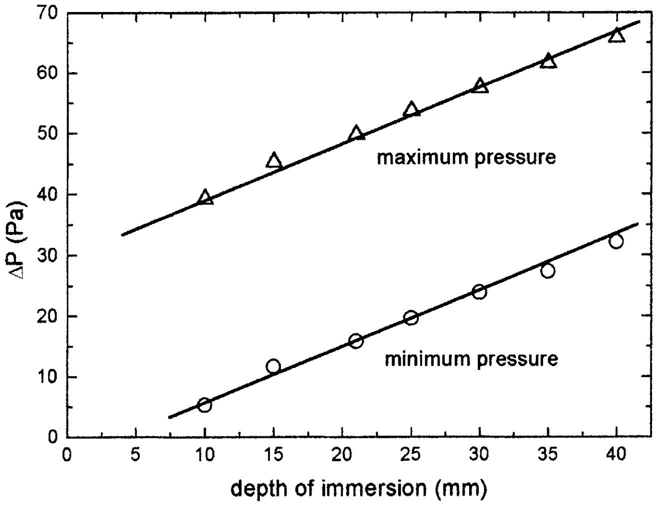

Fig. 4 Maximum and minimum pressure during bubble formation as a function of the depth of immersion for water at room temperature

and γ is clear and sensitive enough to cover the typical γ range of aqueous surfactant solutions. This procedure, together with the experimental set-up shown in Fig. 1, allows the changes in the surface tension to be followed directly in stirred reactors. The γ values obtained are more apparent values (γ_{app}) under the particular experimental conditions than exact surface tensions. Consequently, this method can be applied when tracing a change in γ is more interesting than exact values. Note that the BPD method allows measurements with larger capillaries than the maximum bubble pressure method where $R/a < 0.05$ is required [12]. Crucial parameters during the measurements are the stirrer speed and the gas pressure or bubble frequency. Figures 5 illustrates that in case of the particular experimental conditions a stirrer speed as high as 120 rotations per minute (rpm) still results in satisfying measurements. The maximum stirrer speed may be increased if an optimized protecting cap around the capillaries is used. The gas pressure is best adjusted so that a bubble frequency of 0,5 s^{-1} results. The data depicted in Figure 6 show that a higher gas pressure (higher bubble frequency) leads to a lower apparent surface tension which is a direct consequence of the nonequilibrium conditions with respect to bubble formation. Note that a low gas pressure can lead to problems during the run if, on feeding, the hydrostatic pressure increases too much and hence bubble formation stops. Compared to the conditions for the differential maximum bubble pressure method [10], where the bubble rate is about 2–4 bubbles per minute, the BPD method works at much higher bubble rates of about 30 bubbles per minute.

Application – surfactant solutions

A first test for the method and the experimental set-up is the tracing of the dissolution of different surfactants. The results depicted in Fig. 7 show that measurements at elevated temperatures inside stirred reactors are indeed possible and that it is also possible to discriminate between different types of surfactants. Firstly, the block copolymer surfactant (SE1030) dissolves more slowly than the low-molecular-weight surfactants (SDS, E30, ECD2930) and, secondly, the final γ values show a distinct gradation. For SDS, E30, ECD2930, and Igepal CO880 these values appear to be very low and are in the range 3–5, 6–10, 15–20 and 20–25 mN m^{-1}, respectively. In contrast, the values for SE1030 are in a reasonable range between 37 and 42 mN m^{-1}, but are also about 10 mN m^{-1} lower than the value measured at room temperature with the Du Nouy ring method. A suitable explanation for these low values is not possible at the moment. One reason may be a different solution state of the surfactants at 70 °C compared to temperatures between 25 and 35 °C where most of the investigations of surfactant properties are usually made. It is interesting to note that a decrease in γ at higher temperatures is reasonable as the surface tension of water has a negative temperature gradient [14], but the magnitude of that decrease in the case of surfactant solutions is only speculation. Independent of the range of the γ values the observed gradation is reasonable. An additional problem with SDS and ECD2930 is that both surfactants contain a hydrolyzable ester bond and hence the corresponding alcohols [15] may also contribute to the low γ values. Note that the ester bond hydrolysis is enhanced not only by elevated temperatures (70 °C in that particular case) but also by the presence of a glass surface [16–18]. This hypothesis is supported by the fact that the γ versus t curves for these two surfactants do not reach a constant value within the duration of the experiments. Furthermore, the results depicted in Fig. 7 reveal a problem of the experimental set-up. The final surface tension is so low

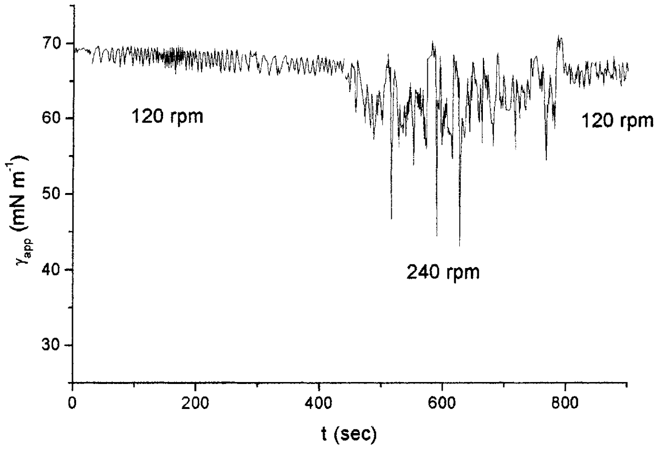

Fig. 5 Influence of the stirrer speed on the measured surface tension of water (70 °C, bubble frequency 0.5 s^{-1})

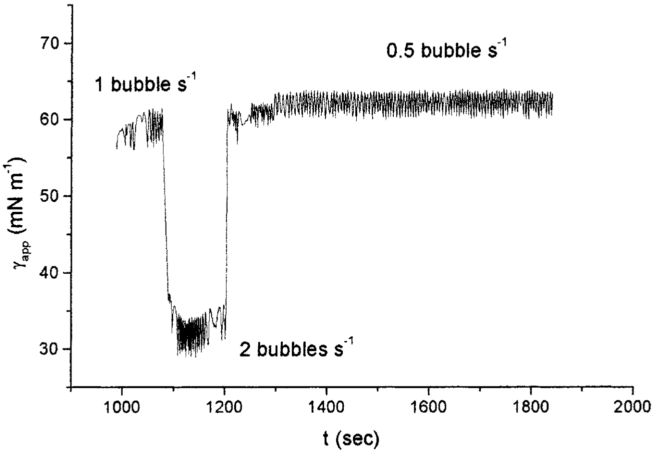

Fig. 6 Influence of the bubble frequency on the measured surface tension of water (70 °C, stirrer is off)

that the gas pressure which was adjusted at the beginning of the experiments to produce a bubble frequency of about 0.5 s^{-1} is too high under these conditions. This leads to an enhanced bubble frequency which causes greater scattering of the data as well as an additional decrease of the apparent γ values (cf. Fig. 6) at higher surfactant concentrations.

In spite of all the problems, these results show that the BPD method is, firstly, sensitive enough to discriminate between different surfactants and, secondly, fast enough to measure on-line changes in γ.

Application – surfactant formation

Another interesting application of the BPD set-up is the tracing of the formation of a surface-active compound during a chemical reaction. The change in γ caused by the formation of 1-octanoic acid during the oxidation of 1-octanol with potassium permanganate according to a recipe described by Bachmann et al. [19] is shown in Fig. 8. As long as the concentration of the caprylic acid is lower than the critical micelle concentration a change in γ is observed which can be used to calculate the reaction rate. The data show that a few minutes after the addition of 1-octanol to the aqueous potassium permanganate solution at $t = 770$ s γ starts to decrease. Until almost 3000 s the rate of the decrease increases due to the solubilizing properties of the caprylic acid already formed. In the vicinity of the critical micelle concentration the changes in γ decelerate again.

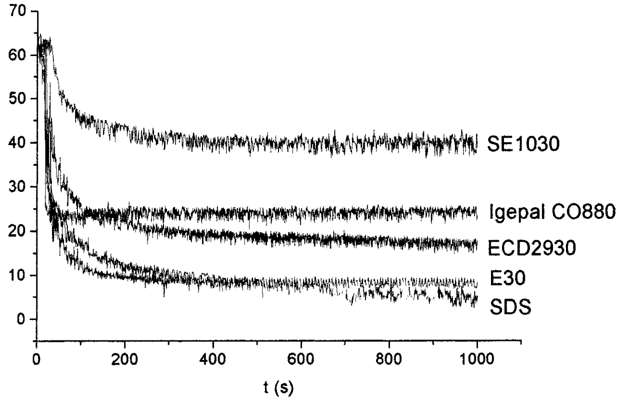

Fig. 7 Change in the surface tension during the dissolution of different surfactants in water (70 °C, 1 g surfactant in each case)

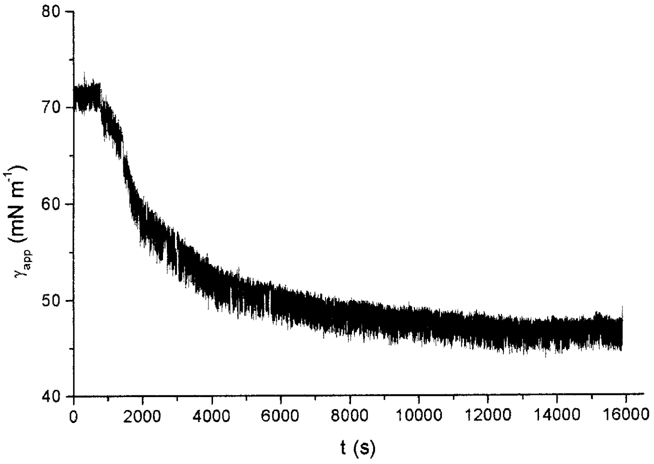

Fig. 8 Change in the surface tension during the oxidation of 1-octanol with $KMnO_4$. Recipe: 250 g water, 2.5 g $KMnO_4$, 2.5 g 1-octanol

Application – emulsion polymerization

A challenging application of the BPD method is to trace γ during a heterophase polymerization to control the level of free stabilizer. A potential benefit of the BPD method is that the desired range of surface tension by active interlinking with the surfactant feed system can be maintained during the growth stage of the polymerization which reflects an optimum stabilizer concentration that is low enough to avoid secondary particle nucleation but high enough to ensure latex stability. This is also important for maintaining reactor stability in the case of continuous polymerizations [9] and for following the consumption of reactive surfactants.

Another benefit of the experimental set-up with respect to heterophase polymerization is that it allows the measurement of the surfactant behavior at polymerization temperatures. Until now, if surfactant properties were needed for modeling emulsion polymerizations, values for room temperature were used although the polymerization temperatures are in most cases almost

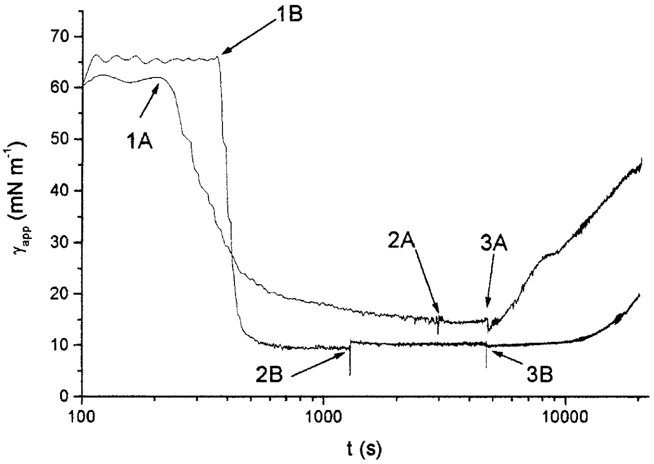

Fig. 9 Change in the surface tension during emulsion polymerizations of styrene (smoothed data). *A*: 1 g ECD2920 as surfactant; *B* : 1 g E30 as surfactant. *1*: surfactant addition; *2*: monomer addition; *3*: potassium peroxodisulfate (*KPS*) addition

50 °C higher. The BPD method can contribute to improving such data sets in the future.

As the aim of this paper is to show the principal possibilities of the application of the BPD method during emulsion polymerization the results presented are limited to batch polymerizations. The data depicted in Fig. 9 represent whole courses of batch styrene emulsion polymerizations from adding the recipe components until the end of the reaction with E30 or the reactive surfactant ECD2930. Again, the BPD method is able to discriminate between the action of different surfactants. Firstly, both surfactants vary in their dissolution behavior (between marks 1 and 2). Secondly, monomer addition does not change the apparent γ values (between marks 2 and 3). Thirdly, during the reaction (after KPS addition at mark 3) the γ versus t curves develop in a completely different way. In the presence of the reactive surfactant the surface tension increases immediately after KPS addition but in the case of polymerization in the presence of E30 γ starts to increase remarkably only after longer polymerization times. The different behavior of γ during the polymerization reflects a different adsorption behavior and possibly also the consumption of the reactive surfactant in the radical polymerization. Alas, it is not possible to discriminate alone with the BPD method between simple adsorption and copolymerization of the reactive surfactant. In the case of nonreactive surfactants an increase in γ clearly reflects an increase in the particle/water interface.

The application of the BPD method during surfactant-free emulsion polymerization started with ionic initiators should allow the detection of surface-active oligomers which are formed in situ. To investigate their formation in the course of the polymerization is of special interest as a lot of suppositions have been made with respect to how these oligomers contribute in particle formation, stabilization, and radical entry during emulsion polymerization [20].

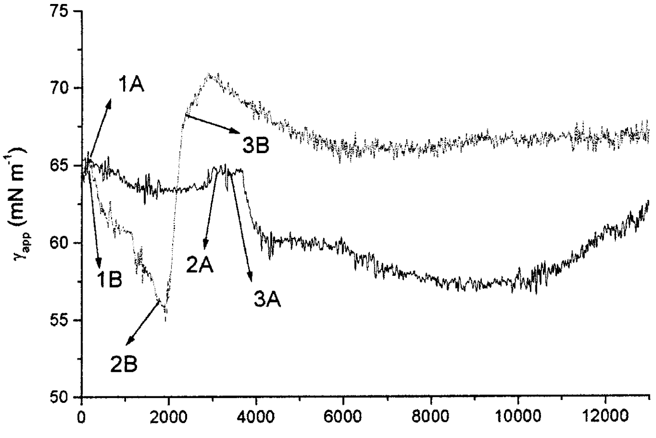

Fig. 10 Change in the surface tension during surfactant-free emulsion polymerizations (smoothed data). *A*: styrene as monomer; *B*: methyl methacrylate as monomer; *1*: monomer addition; *2*: KPS addition; *3*: visible turbidity

The development of γ in the course of the surfactant-free emulsion polymerization of styrene and MMA, respectively, is depicted in Fig. 10. At the beginning of the reaction both systems behave in a different way. After monomer addition γ decreases much more in the case of MMA polymerization (run B) than during styrene polymerization (run A). The reason for this behavior is the higher MMA concentration which is soluble in the aqueous phase. After adding KPS (at marks 2A, 2B) γ increases by almost 15 mN m^{-1} during run B within a few minutes due to the consumption of the monomer by aqueous-phase polymerization. In contrast, styrene polymerization showed that γ practically does not change during this period. A couple of minutes after the reaction mixtures becomes visibly turbid at marks 3A and 3B (run B after 9 min, run A after 4 min) the surface tension starts to decrease. During styrene polymerization γ decreases more than during MMA polymerization which is a consequence of the lower surface activity of the MMA oligomers due to their higher polarity. The γ versus t curves again show an increase at higher polymerization times and additionally oscillatory behavior is indicated especially during styrene polymerization. It is interestingly to note that these results are not that much different from off-line surface-tension measurements at room temperature during surfactant-free styrene emulsion polymerization with a slightly different recipe. In that particular case γ values oscillating between 45 and 70 mN m^{-1} with advancing polymerization time were measured with the Wilhelmy plate method [21].

These very first results permit at least two conclusions to be drawn with respect to the mechanism of surfactant-free emulsion polymerization. Firstly, nucleation occurs at very low oligomer concentrations since the γ measurements allow the consumption of the monomer to be traced (run B) but not the formation of surface-active oligomers during the prenucleation period: this is in agreement with previous experimental results [22, 23]. Secondly, the decreasing surface tension during the particle-growth period indicates that surface activity of oligomeric species does not inevitably lead to an entry into latex particles as was postulated [24].

Conclusions

The BPD method is a robust method for measuring on-line the surface tension of solutions and dispersions even in stirred reactors at any temperature. The method is based on the finding that the difference between the maximum (hemisphere and bubble diameter corresponds to the capillary diameter) and the minimum pressure (bubble escape from the capillary) during bubble formation correlates strongly with the surface tension of the surrounding solution. The measured values are apparent values and, hence, the method is of special value if changes in the surface tension are more important than exact values. Nevertheless, the BPD method is sensitive enough to discriminate between different surfactants to trace surfactant dissolution as well as the formation of surface-active compounds during chemical reactions. Furthermore, it is possible to trace surfactant consumption during emulsion polymerization and to follow the formation of surface-active species in the course of surfactant-free emulsion polymerization. Future work will especially focus on the improvement of the experimental set-up with the goal of allowing measurements at higher stirrer speeds. Another important topic will be more detailed investigations of emulsion polymerizations which allow the control of the surfactant feed in such a way that the surface tension is kept at an optimum level during the growth stage.

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