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Online-Analysis on Acoustically Levitated Droplets

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Summary: Aqueous solutions of acrylic acid were levitated in a 40 kHz acoustic levitator. The monomer amount in the levitated droplets was monitored by Raman spectroscopy relating to an internal standard. Thus evaporation of the monomer as well as polymerization reactions initiated by a redox system were investigated by Raman spectroscopy and resultant data were compared to HPLC data. Decreases in monomer amount due to evaporation can be clearly distinguished from polymerization reactions. Additionally, temperature measurement within the droplet throughout a polymerization reaction shows the typical temperature course originating from the heat of polymerization.

Keywords: acoustic levitation; acrylic acid; online; polymerization; Raman spectroscopy

Introduction

Aerosols are involved in several industrial processes such as spray drying and spray polymerization. Experimental data corresponding to the processes in the dispersed phase are difficult to obtain because the particles are moving fast and on varying trajectories in the reactor or dryer, respectively. Analysis of moving droplets can be avoided by carrying out single droplet experiments in a levitator. Levitation enables containerless positioning of objects "freely suspended". Depending on the material properties and the size of the object, levitation can be achieved through different force fields: optical, magnetic, electrostatic, aerodynamic and acoustic.

Levitated droplets provide the possibility of in-*situ* investigation of aerosol physics and chemistry. To date, especially evaporation kinetics of levitated droplets have been studied theoretically[1] and experimentally.[2] During the evaporation process, a camera can not only constantly observe the droplet size, but the morphology of the droplet or the remaining particle can be determined as well.[3] Beyond evaporation kinetics, the chemical composition of reactions taking place in levitated droplets can also be monitored by spectroscopy.[4] However, applying spectroscopic methods to levitated droplets presents several difficulties, e.g. aligning the probe to focus on a single droplet. Furthermore, liquid droplets are subject to evaporation due to the large surface-to-volume ratio. Thus particle size can undergo a significant change, possibly resulting in a particle smaller than the spectroscopic focal point. In this work, a newly constructed acoustic levitator based on a 40 kHz ultrasonic transducer will be presented. Raman spectroscopy is used to monitor the chemical composition in the levitated droplets using an internal standard to overcome the problems described above.

Principle of Acoustic Levitation

In order to levitate droplets with diameters in the range of micrometers up to a few millimeters, acoustic levitation is the most appropriate method to use. An acoustic levitator consists mainly of an ultrasonic transducer and an opposite reflector. By adjusting the distance (d) between the transducer and the reflector a standing

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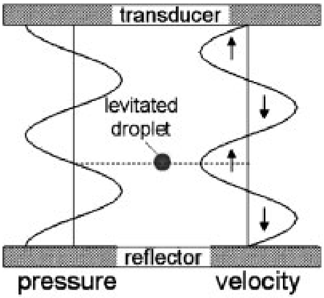

Figure 1.
Pressure and velocity distribution of a standing acoustic wave with the position of a levitated droplet.

ultrasonic wave can be generated. Therefore, d has to be

$$d = n \cdot \frac{\lambda}{2} \qquad (n = 2, 3, 4 \ldots)$$

where λ is the wavelength of the acoustic wave. Pressure distribution and corresponding velocity distribution of a standing wave are shown in Figure 1. Droplets or particles respectively introduced into the standing ultrasonic wave are affected by a force towards the nearest pressure node and are levitated as the ultrasonic radiation force compensates gravity.[5]

Description of the Acoustic Levitator

An acoustic levitator based on a 40 kHz ultrasonic transducer has been constructed as schematically shown in Figure 2. The ultrasonic transducer is fixed opposite to a concave reflector. By moving the reflector, which is connected to a micrometer adjustment screw, the distance between the sonotrode and the reflector can be defined. It can be varied between 0 mm and 38 mm. With a wavelength of 8.6 mm (20 °C) it is possible to provide eight pressure nodes at most. In the majority of experiments a sonotrode - reflector distance providing two to four pressure nodes is used.

Droplets containing monomer solution are inserted into one of the pressure nodes by using a syringe with a thin cannula (e.g. 0.4 mm of diameter) to limit adhesion by a minimal contact area. A levitated droplet with a typical diameter of about 1.5 mm is shown in Figure 3.

Quantitative Raman Spectroscopy

A 785 nm Raman spectrometer is used for quantification of the monomer in the levitated droplets. Raman spectra are obtained

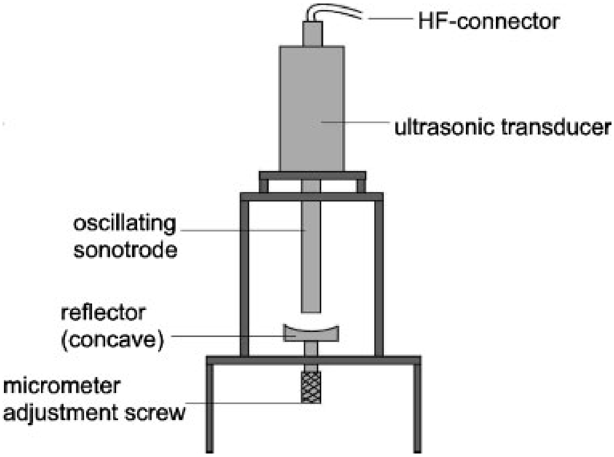

Figure 2.
Diagram of the acoustic 40 kHz levitator.

Figure 3.
Levitated droplet with a typical diameter of about 1.5 mm.

by non-contact online measurements and are evaluated by applying a PLS (partial least squares) model for quantitative analysis. The monomer concentration is proportional to the intensity of the corresponding Raman bands. However, because constant measurement conditions cannot be guaranteed, (e.g. because of a change in particle size) a Raman-active internal standard is used to compensate for intensity variations. Figure 4 shows the Raman spectra of the monomer acrylic acid (1), the internal standard phenol (3) as well as a mixture of both (2). The aromatic ring vibration of phenol causes the band at a wave number of 1003 cm^{-1}. Since the acrylic acid spectrum does not show a band at exactly this wave number, the aromatic vibration band is used for normalization. Because the band of acrylic acid at 980 cm^{-1} overlaps the aromatic band at the edge, the band area is not suitable for normalization. Consequently, spectra of reaction mixtures containing acrylic acid and phenol are normalized by the height of the aromatic band. Thus the amount of acrylic acid obtained by Raman spectroscopy is related to the internal standard expressed as the molar ratio $n_{acrylic\ acid}/n_{phenol}$ or the mass ratio $m_{acrylic\ acid}/m_{phenol}$ respectively.

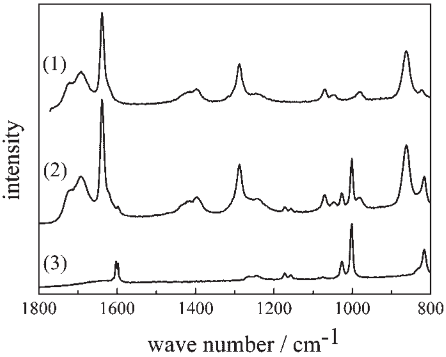

Figure 4.
Raman spectra of acrylic acid (1), phenol (3) and a mixture of both (2).

Experimental Part

A droplet of aqueous solution containing acrylic acid and phenol is inserted into a pressure node of the acoustic levitator by a syringe. The amount of monomer (acrylic acid) and internal standard (phenol) is monitored by online-Raman spectroscopy. In the meantime, liquid, e.g. containing an initiator, can be added to the levitated droplet. After a certain period of time, ten to thirty minutes, the sample is removed from the levitator using a glass capillary and is diluted with scavenger solution containing hydroquinone as an inhibitor. The residual monomer, as well as the amount of internal standard can be determined by HPLC methods.

Raman Spectra of Levitated Droplets

In order to determine the feasibility of Raman spectroscopy on levitated droplets, the first experiment presented was carried out without adding initiator. An aqueous solution containing acrylic acid (74.4 weight %) and phenol with a mass ratio $m_{acrylic\ acid}/m_{phenol}$ of 14.4 is levitated and monitored by Raman spectroscopy. The above described evaluation of the Raman data results in the time dependent mass ratio of monomer and internal standard.

Four different droplets were introduced, monitored and removed within 65 minutes. Figure 5 shows the normalized Raman spectra of the first sample. The bands, e.g.

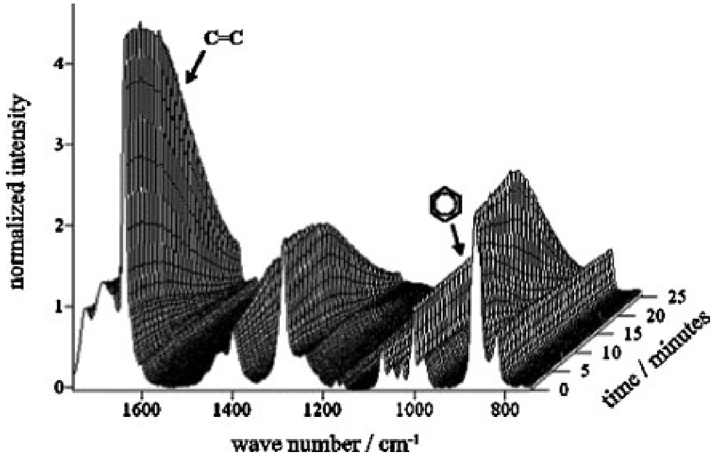

Figure 5.
Normalized Raman spectra of a solution that originally contained 74.4 weight % acrylic acid with a mass ratio to phenol of 15.4. No initiator was used.

1003 cm^{-1} and 816 cm^{-1}, originate from the phenol as an internal standard and their intensity remains constant throughout the spectra. The bands of acrylic acid (e.g. vinyl band at 1641 cm^{-1}) shrink gradually, which represents the evaporation of acrylic acid. This course is diagrammed in Figure 6 and shows not only the resulting mass ratios evaluated from the Raman spectra but the initial mass ratio of the monomer solution as well. Also shown are the HPLC data derived from measurements after removal of the particle from the acoustic levitator. The results from Raman measurements are confirmed by the initial mass ratio of the solution as well as the HPLC data.

Besides the evaporation process, polymerization reactions can also be monitored. The redox initiator system hydrogen peroxide, Brüggolit™ FF6 and $FeSO_4$ was

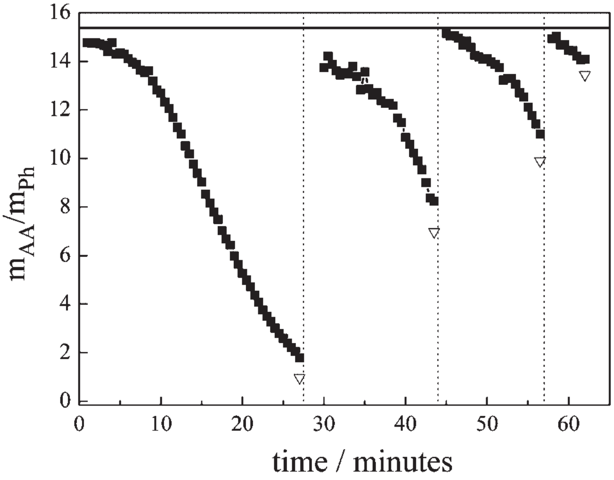

Figure 6.
Mass ratio of acrylic acid (AA) to phenol (Ph) as determined by Raman spectroscopy (■), HPLC (▽) and initial weight (plain line, -). Four different droplets were deployed, monitored and removed within 65 minutes. The solution initially contained 74.4 weight % acrylic acid with a mass ratio to phenol of 15.4. No initiator was used.

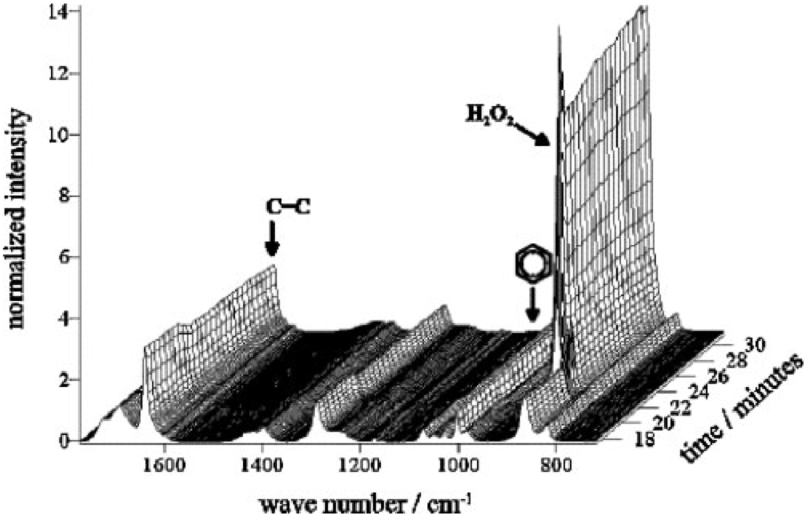

Figure 7.
Normalized Raman spectra of a solution initially containing 33.1 weight % acrylic acid with a mass ratio to phenol of 11.1. The reducing components of the initiator mixture were present in the monomer solution and the oxidizing agent, H_2O_2 (solution of 30 weight %), was added at 21 minutes.

used at room temperature to generate radicals, with $FeSO_4$ being applied only in catalytic amounts. While Brüggolit^{TM} FF6 and $FeSO_4$ were initially present in the monomer solution, the oxidizing component hydrogen peroxide was added after the droplet of monomer solution had already been inserted into the levitator. The resulting data of two polymerization experiments can be seen in Figure 7 to Figure 10. While Figure 7 and Figure 9 show the normalized Raman spectra of one of the investigated droplets, Figure 8 and Figure 10 show the course of the mass ratios of four different droplets each. The presented experiments differ mainly in the concentration of the added hydrogen peroxide solution which is with 30.0 weight % much higher in the first case (Figure 7 and Figure 8) than in the second reaction (Figure 9 and Figure 10) with 1.3 weight %. The high excess of H_2O_2 can be seen in the normalized Raman spectra of Figure 7. The H_2O_2 band appears intensely at 21 minutes immediately after the addition of the H_2O_2 solution to the levitated monomer droplet. At the same time, bands originating from acrylic acid show a sharp decrease in intensity, thereby indicating a reaction. The course of the mass ratio (Figure 8) undergoes a sudden change when the oxidant is added, while before and shortly after initiation of the reaction the evaporation of acrylic acid is

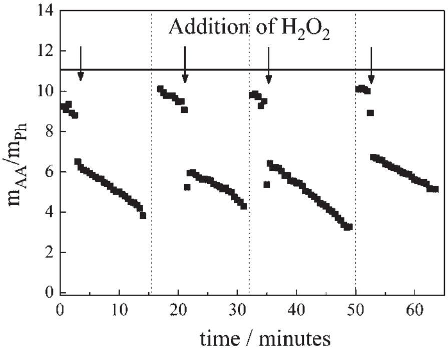

Figure 8.
Mass ratio of acrylic acid (AA) to phenol (Ph) as determined by Raman spectroscopy (■) and initial weight (plain line, -). Four different droplets were deployed, monitored and removed within 65 minutes. The solution initially contained 33.1 weight % acrylic acid with a mass ratio to phenol of 11.1. The reducing components of the initiator mixture were present in the monomer solution and the oxidizing agent, H_2O_2 (solution of 30 weight %), was added at the marked time (↓).

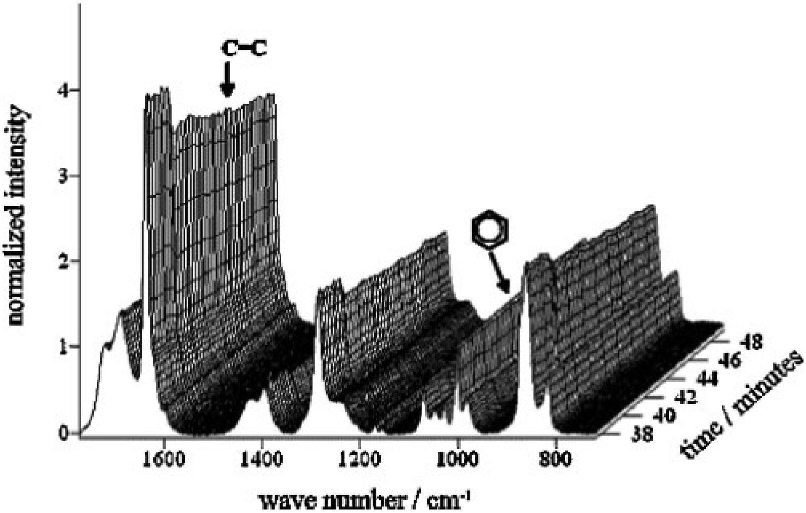

Figure 9.
Normalized Raman spectra of a solution initially containing 46.7 weight % acrylic acid with a mass ratio to phenol of 13.8. The reducing components of the initiator mixture were present in the monomer solution and the oxidizing agent, H_2O_2 (solution of 1.3 weight %), was added at 40 minutes.

monitored. Subsequently, the mass ratio shows a superposition of the polymerization and the evaporation.

The use of the less concentrated H_2O_2 solution results in a similar course of the mass ratio $m_{\text{acrylic acid}}/m_{\text{phenol}}$ and the final value is confirmed by HPLC data (Figure 10) and corresponding Raman spectra. Although the addition of oxidant is not visible in the normalized Raman spectra (Figure 9), a rapid decrease of acrylic acid can be detected in the band intensities and the resulting mass ratio (Figure 10). As expected, the decrease in mass ratio attributed to the polymerization reaction amounting to 17% in average was much smaller than the conversion initialized by the higher concentrated H_2O_2, which was 30% in average.

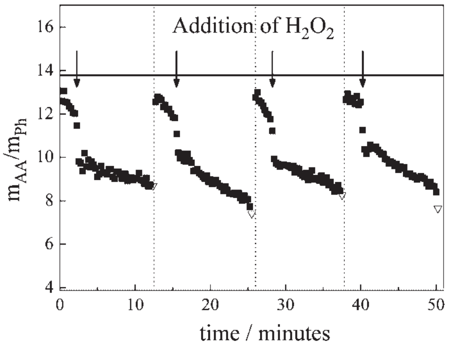

Figure 10.
Mass ratio of acrylic acid (AA) to phenol (Ph) as determined by Raman spectroscopy (■), HPLC (▽) and initial weight (plain line, -). Four different droplets were deployed, monitored and removed within 50 minutes. The solution initially contained 46.7 weight % acrylic acid with a mass ratio to phenol of 13.8. The reducing components of the initiator mixture were present in the monomer solution and the oxidizing agent, H_2O_2 (solution of 1.3 weight %), was added at the marked time (↓). Evaluation of Raman data shown in Figure 9 results in the fourth curve.

Temperature Course During Polymerization in a Levitated Droplet

The course of polymerization is not only visible by a decrease in the amount of monomer but also by a peak in temperature. The temperature was measured by placing a thermocouple (∅ 0.5 mm) into the levitated droplet. Figure 11 displays the course of temperature in the pressure node used for levitation. Beginning with the

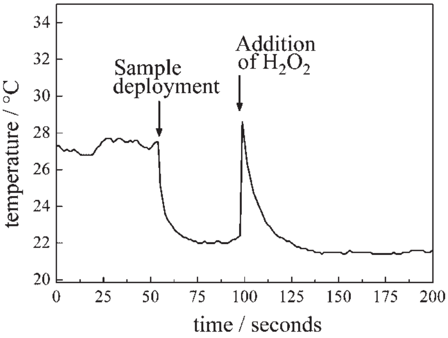

Figure 11.
Temperature course in a levitated droplet during a polymerization reaction measured by a thermocouple. The monomer solution containing 46.7 weight-% acrylic acid and the reducing agents of the initiator mixture was deployed into the pressure node at 54 s. The oxidizing component H_2O_2 (solution of 1.3 weight %) was added at 97 s.

ambient temperature of about 27 °C, the temperature falls to 22 °C after the deployment of acrylic acid solution that contained the reducing initiator components (Brüggolit^{TM} FF6, $FeSO_4$) plus the monomer. Upon completion of the initiator system by addition of hydrogen peroxide, the polymerization reaction is indicated by a sharp increase in temperature followed by a decrease to the former temperature. Thus, the recorded temperature within the droplet shows the typical temperature peak of polymerization reactions.

Conclusion

Raman spectroscopy using an internal standard was successfully use to analyze levitated droplets of acrylic acid solution. The amount of monomer in the levitated droplets was monitored undergoing evaporation and polymerization simultaneously. Both of these processes can be clearly distinguished from one another by different slopes of the mass ratio curve. The mass ratio evaluated from the Raman spectroscopy was confirmed by HPLC data. In addition to online-monitoring of the monomer amount, the course of temperature in the levitated droplets was measured during a polymerization reaction. The increase in temperature represents the rate of heat generation during polymerization.

[1] A. L. Yarin, G. Brenn, O. Kastner, D. Rensink, C. Tropea, *J. Fluid Mech.* **1999**, *399*, 151.
[2] O. Kastner, G. Brenn, D. Rensink, C. Tropea, *Chem. Ing. Tech.* **2000**, *72*, 862.
[3] S. Sacher, G. Krammer, *Chem. Ing. Tech.* **2005**, *77*, 290.
[4] J. F. Lübben, B. Schrader, *J. Mol. Struct.* **1997**, *410–411*, 543.
[5] E. G. Lierke, *Acustica* **1996**, *82*, 220–237.