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New micro viscosity sensor—A novel analytical tool for online monitoring of polymerization reactions in a micro reaction plant

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ABSTRACT

The authors developed within a project funded by the German government a micro reaction plant which allows to produce polymers out of up to 8 monomers by using the Suzuki coupling method. Micro reactors can have a positive influence on the quality of the polymer product. Especially the mixing quality of the monomers, the catalyst solution, and end capper solutions have a great influence on the molecular weight distribution. With micro reactors it is possible to have a very narrow distribution which is not achievable in typical batch processes. To monitor the product quality a new sensor was developed to measure online the product viscosity and with this the molecular weight of the polymer.

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1. Introduction

During the last 15 years, it has been shown that micro reactors can help to develop new and optimize conventional chemical reactions [1]. Different micro mixers, micro heat exchangers, micro reactors for homogeneous or heterogeneous liquid–liquid reactions or for gas/liquid reactions have been developed and tested for development as well as for production. Even the handling of solids, e.g. manufacturing of particles or polymerization reactions could be shown.

Very important for running micro reactors is the detection of the products formed during the process. This is necessary to optimize the reaction as well as to control the process during a production. Even though a variety of different reactions in micro reaction plants could be realized, still not many online analytical methods for micro reactors are known.

Within the mentioned project it was necessary to develop a method to control the chain length of the produced polymer. During the polycondensation of the monomers the viscosity of the solution changes. The higher the chain length and therefore the polymer concentration in the solvent, the higher becomes the viscosity of the solution. Therefore, it was decided to use this parameter as a signal to follow the reaction. With this new analytical method it is possible to monitor the reaction and control the chain length and molecular weight distribution.

Different types of rheometer are available at the market. In a classic rheometer the dynamic viscosity is measured by means of shear forces which occur when a plate or cylinder is rotating against a fixed counterpart. Alternatively capillary viscosimeters can be used. Here a liquid is forced through a tube with a constant cross-section and known dimensions. Either the flow-rate or the pressure drop is fixed and the other measured. Knowing the dimensions, the flow-rate can be converted into a value for the shear rate and the pressure drop into a value for the shear stress. This can be used to calculate the dynamic viscosity. Both analytical tools require to take a sample from the product and are therefore not working in a continuous mode [2].

Even though the viscosity of small volumes can be measured with a classical rheometer, this analysis cannot be performed "online" during production. On the other hand, online analysis can be performed with conventional viscosity sensors. However, large flow-through volumes are required. Therefore, the project presented here combines online analysis with the handling of small volumes and flow-rates as used within micro reaction plants.

The following polycondensation reaction (Suzuki reaction) was investigated within the project (Fig. 1). The developed viscosity sensor had to monitor the product quality during the production in a micro reaction system and stop the reaction at a certain point.

The monomers M1 and M2 were mixed with the palladium catalyst solution, bases and end cappers, leading to a two-phase

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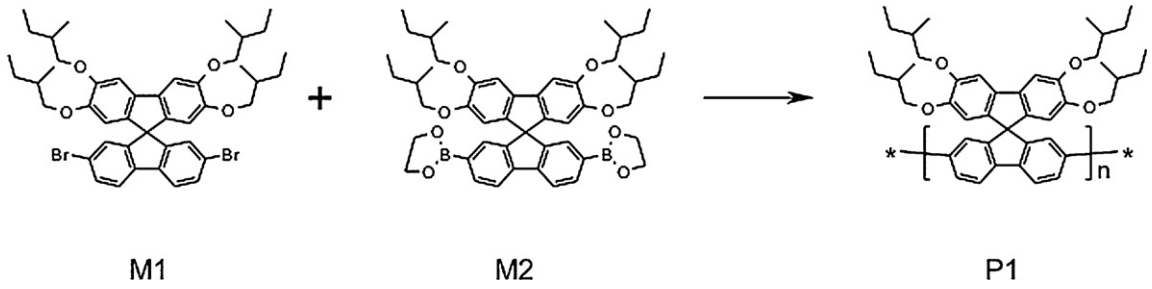

Fig. 1. Reaction scheme polycondensation [3].

reaction mixture. One of the major tasks within the micro reactor was to keep a homogeneous emulsion over the complete reaction time of approx. 30 min. The temperature range was between 70 °C and 150 °C. For this special product which is a dye for an Organic Light Emitting Diode (OLED) our project partner Merck (former Covion) was looking for a very narrow range of molecular weight distribution. The idea was to monitor the complete process over time by viscosity to stop the reaction at a certain point, when the target in molecular weight was reached. One difficulty is the non-linear time behaviour of a polycondensation. In contrast to a "polymerization" the "polycondensation" shows a slow increase of the chain length in the beginning, and a very fast increase close to the end of the reaction. Therefore, the sensor has to be very sensitive and has to show a fast response to changes in the solution.

For the preliminary investigations of the technology different ideas have been discussed how to measure viscosity in a continuous flow system with very small volumes (below one millilitre). One idea was to use the surface acoustic waves (SAW) principle [4]. In this case, acoustic waves are generated in the surface of a piezo crystal with an electrode structure. Emitter and receiver are placed across with a clear area in between above which the acoustic surface waves can run. To direct the waves on the surface another layer is applied which has a lower sonic velocity as the substrate. Based on this a two dimensional wave guide is created (Fig. 2). One can run the liquid probe over this surface and measure the resonance frequency and amplitude of the response signal which is depending on the product from viscosity and density of the probe material.

Using different polyethylene glycol (PEG 20000) dilutions with an increase of molecular weight of probe material we were able to see an increase of the sensing signal. The same effect could be shown with glycerine solutions. In general this signal was proportional to the weight proportion but for PEG not linear and above a certain concentration independent from the chain length and therefore the viscosity (Fig. 3). This means that from a certain point the signal was not increasing anymore. One explanation of this effect might be the very little penetration depth of only 0.1 μm at an excitation frequency of 140 MHz. Thereby only substrings of the molecule interact with the surface. Furthermore the very fast occurring surface contamination and problems with the temperature stability lead to the decision not to pursue the concept further. Even if the advantages of this technology were the well-established electronics/measuring system in combination with the existing know-how of data analysis.

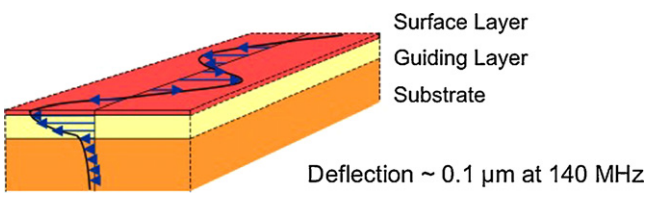

Fig. 2. Outline SAW sensor.

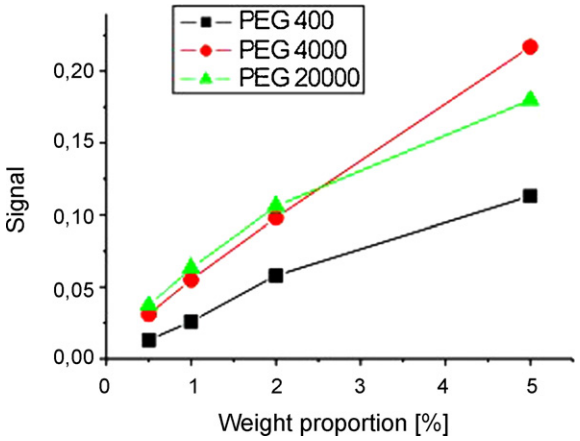

Fig. 3. SAW signal for PEG as function of weight proportion.

The second experimental set-up was using an oscillating tube as a measurement tool. By using an electro-magnetic field, the tube is forced to oscillate (Fig. 4). The resonance frequency of this process depends on the mechanical parameters and the geometry of the tube and was here in the range of 6–20 kHz. This resonance frequency is damped by the liquid which runs through the tube. The damping is depending on the viscosity of the test liquid. This effect can be used as measuring signal. In addition at this frequency a higher penetration depth can be achieved which makes this set-up less sensitive against surface contaminations than the SAW set-up. For this set-up a coil is applied on the outer wall of a tube and then this tube is placed within a magnetic field. By the permanent magnetic field Lorenz forces are induced at the coil and the tube is forced to torsion. By varying the excitation frequency, the resonance frequency can be measured with the aid of an impedance

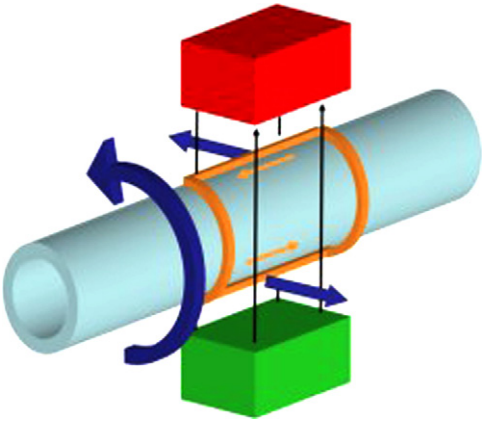

Fig. 4. Principle oscillating tube [5].

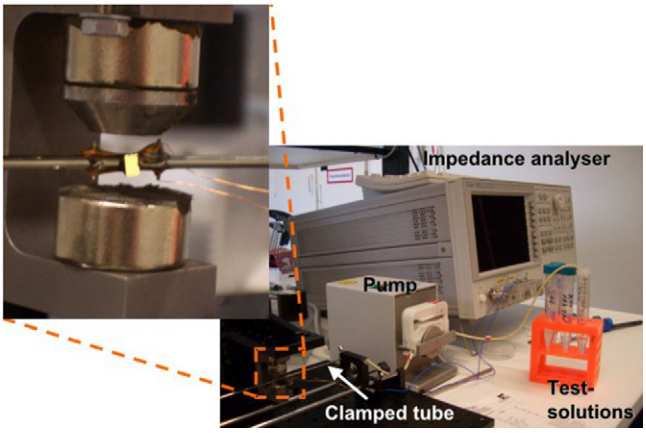

Fig. 5. Test set-up.

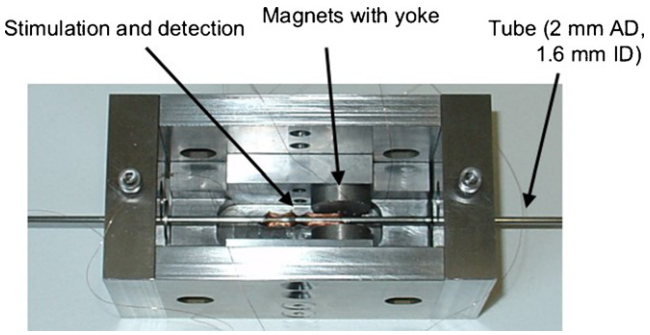

Fig. 6. First prototype of micro viscosity sensor.

analyser. Whereas the impedance $|Z|$ of the coil is a measure of the resonance.

Above and below the tube magnets are fixed and the tube is placed between these magnets. The tube is fixed in a mechanical very stable rack so that it cannot be distorted from the outside. Furthermore, a peristaltic pump has been used to pump the test solution through the tube. With this set-up the first test series were performed using an impedance analyser (Fig. 5). With changing content of PEG or glycerine the resonance frequency and amplitude is changing. When this is converted either in density or viscosity one can see a linear behaviour. But again for PEG at a higher viscosity the signal is not completely linear (Fig. 7).

Based on these results a first prototype was produced. The outer dimensions were 90 mm × 45 mm × 45 mm. The stainless steel tube had an outer diameter of 2.0 mm and an inner diameter of 1.6 mm (Fig. 6). This tube again was fixed between two magnets with yoke. In the first step just a single coil was applied and used for excitation and in a subsequent step measured. In the following, two coils were used: one for excitation and one for detection. With this change a much faster detection and better signal-to-noise ratio was possible. Based on this improvement also the electronics became more simple.

To measure the first calibration lines different dilution series based on Cannon N100 oil have been prepared by the project partner hte and the viscosity was controlled by a standard rheometer. A series of different solutions with an increasing weight percentage of PEG 20000 or glycerine (both from Merck) in water was tested. The viscosity range was up to 3500 mPas at room temperature and dropped down to 1000 mPas at 80 °C. It could be shown that the results of the new developed sensor fit quite well with the comparative data. There are two parameters which can be used to calculate the viscosity: the amplitude and the frequency of the resonance oscillation. The higher the viscosity the lower the amplitude and the higher the resonance frequency. The two upper diagrams in

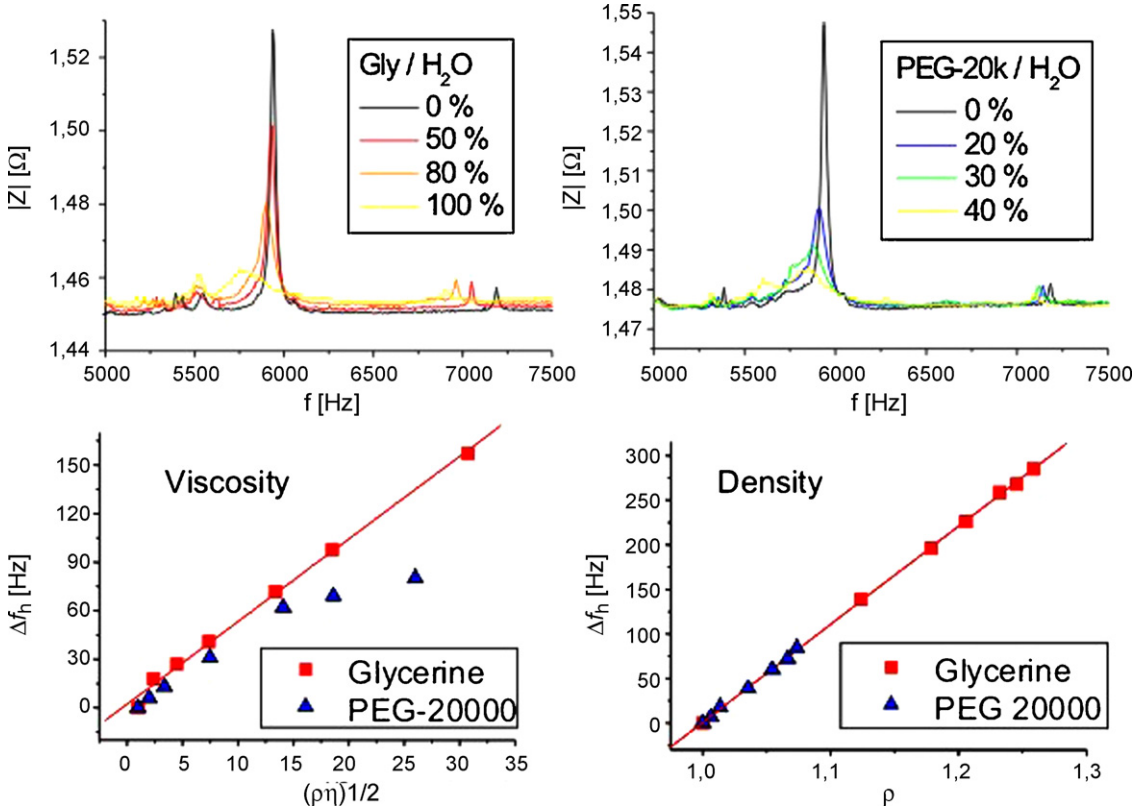

Fig. 7. Measurement data for calibration.

Fig. 7 show the amplitude plotted against the frequency. The two lower diagrams show the frequency shift Δf_h plotted against the density/viscosity product and the density. This was chosen to get a linear behaviour with which one can calculate the viscosity based on the known density. For low viscosities, the amplitude gives a good resolution. The frequency is used for higher viscosities. To broaden the range over which you can measure continuously both signals can be used.

With the first generation of the electronics the resolution in viscosity was only in the range of 30–40 mPas with a high standard deviation. To improve this, the set-up was changed to a so-called phase-locked loop (PLL) configuration. The PLL electronics is an oscillator which uses a phase comparator to synchronise on a reference frequency. With this set-up a much better signal resolution with low standard deviation was achieved.

One of the drawbacks still was that when you switch the flowrate of the systems it needs some time to adjust the signal. Also when between very different viscosities is switched the system needs time to adjust. This was an issue which should be further investigated. But in general the sensor set-up shows a good response and is quite stable in the general set-up.

Different geometric configurations have been designed. Within the German industry consortium MicroChemTec standard geometric interfaces of micro reactors and the related equipment have been defined [6]. The very first prototype was build with outer dimensions of 90 mm × 45 mm × 45 mm. This is the footprint of the so-called "backbone" construction kit which was a result of the standardisation. To further minimise the probe volume and outer dimensions of the total sensor housing the second generation was only 65 mm × 30 mm × 30 mm. The tube OD was reduced to 1/16″ and 1.2 mm inner diameter. This leads to a probe volume of only 75 μl.

Another important result of the investigations was that the viscosity is strongly depending on the temperature. To overcome this effect a set-up was designed to pre-heat the solution prior to measurement. A base plate is electrically heated with an integrated heat exchanger to stabilize the inlet temperature. After that the solution is fed into the sensor tube. The integrated electronics had to be encapsulated to work at temperatures of up to 80 °C, the reaction temperature in the plant.

2. Conclusions

Different methods to measure the viscosity online in a continuous flow system have been investigated. It could be shown that the oscillating tube is the most promising approach regarding stability and ease of use. A compact sensor set-up and the required electronics have been developed, fabricated and tested. To overcome the temperature influence on the viscosity it was necessary to integrate a pre-heater to work on a stable temperature. The electronics offer different output signals so that the sensor can be easily integrated into an automated process control system. With this new sensor it is possible to measure online the molecular weight during a polycondensation reaction. Using this signal it is possible to develop the respective processes and control the production process.

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