

## **Polymerization in sprays – one step from a monomer to a powder polymer**

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### **Abstract**

Spray drying of powder polymers is a common technique to generate well defined polymer particles in shape and size. To have a good solid handling spherical particles in a size range of 10 to 1000  $\mu\text{m}$  are usually desired. The whole process seems to be standard processing but even the first step, the atomization, could be a bottle neck as we found out in our research. In particular the handling of the atomization is mostly dependent on the molecular structure of the polymer and length of polymer chain. The molecular weight of the polymer has a big influence on the rheological behavior of the solution, if it appears as non-Newtonian fluid with passing a critical concentration. Consequently the rheology of the fluid to be atomized has a big impact on the atomization behavior. Results on spray drying polyvinylpyrrolidone (PVP) solved in water show a change of morphology from particles to filaments with increasing molecular weight and concentrations of the polymer. This relation between molecular weight and atomizing behavior is also important for the current research where a polymerization will take place in sprays.

The spray drying of a reactive system is focus of this research. Here the former described spray drying process is expanded with an additional step, the polymerization or reactive step. Thus, a reactive monomer or partial linked monomer solution is atomized in a modified spray dryer. By decomposing a thermal starter in the fluid the monomer forms chains and consequently polymers. This starter is decomposed under certain kinetics by the drying gas or by the thermal input of a special 3-fluid nozzle (see following passage). The use of this nozzle is necessary because of the aim for optimal utilization of the small retention time within a spray dryer.

The coupling of starter, polymerization and drying kinetics is of special interest within our research. The model substances are water soluble monomers, salts of acrylic acid, and a radical thermal starter, an azo compound. The special tool for controlling starter and polymerization kinetics is the 3-fluid nozzle. This nozzle has three different feeds for the starter solution, monomer solution and the atomization gas, e.g. nitrogen. All feeds are mixed in- or outside the nozzle. In addition the nozzle has a double jacket for keeping a constant temperature inside the nozzle. The presented results show the influence of retention time of the fluids within the nozzle on the degree of polymerization at the nozzle tip. The optimal parameters for setting the start of the polymerization around the nozzle tip are presented. At this optimum a successful droplet formation is guaranteed, non-Newtonian effects are prevented and simultaneously completely polymerized particles with a certain molecular weight are generated in the process' downstream.

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### **Introduction**

Water soluble polymers have a wide application field in pharmaceutical, cosmetics and chemical industry used as additives in drugs, as hair styling products or as cleaning agents. Mostly powder polymers are preferred because of its advantageous properties concerning further processing, transport and storage. To gain powder polymers a lot of processing steps are necessary. After the polymerization in one or more reactors some formulation processes, e.g. drying, agglomeration and milling are required to produce a powder polymer. The combination of these different processes in a single process, called one-step-process is obvious and theoretical described e.g. in US patent from 1993 [1]. Based on this and familiar patents Krüger adopted this new process concept and called it spray polymerization. He investigated the generation of superabsorbent polymer particles in droplets during their forced flow through a vertical heated pipe reactor [2]. Previous works showed that efficiency and yield of the reactive spray polymerization are key problems and have to be investigated further. Thus, a new engineering of the one-step-process and a detail understanding of the kinetics of the polymerization is focus of this research.

The main aggregate of the new concept is a common spray dryer. It combines three different sub-processes, atomization of the liquid to small droplets in a hot gas, drying and solid formation of the dispersed droplets, and finally the separation of the dried particles from the aerosol. Consequently the atomization of a reactive liquid is an addition of another sub-process, the polymerization within the droplets. The short retention time in a spray

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dryer requires a very intensive reaction with fast polymerization kinetics. Subsequently a high amount of exothermic energy is set free and safety problems are to be taken into account.

Therefore the spray polymerization process is based on the radical polymerization of acrylic acid and its acrylates. Krüger also used these reactants because of the fast growing rates [2]. The advantage of the acrylates is that they can't evaporate during the drying process.

The knowledge about the effects of the different sub-processes individually or in competition to each other is necessary for the whole spray polymerization process and to guarantee an effective production of well defined particles in size and shape.

The pretreatment of the reactive liquid and its atomization is subject of the presented work. An optimal pretreatment of the liquid has to be guaranteed so that the start of the polymerization is done before the liquid's atomization. The starting kinetic is mostly dependent on the decomposition of the starter, which is also a function of temperature and time. If there is no or insufficient pretreatment, the retention time in the spraying process won't suffice to form polymers in the droplets. The yield of the process decreases because of the evaporation of a high amount of atomized monomer at the process starting. The efficiency also decreases because of the evaporation of the solvent. A limitation of the monomers mobility could occur that terminates the polymerization. Here kinetics of the initiator and of the reaction have to be considered. A special 3-fluid nozzle is designed to investigate the effect of the retention time of the reactive liquid within the nozzle concerning to the atomization behavior outside the nozzle. To get information about the effect of the pretreatment before atomization it is important to find out how oligomer or molecules with a higher polymerization degree effect the atomization. First droplet size distributions are measured on different water soluble polymers with varied molecular weights. All measurements are done with a pneumatic nozzle. The advantage is, compared to other nozzles, the handling of higher viscous fluids because of the great impact of the high velocity gas used to atomize the liquid. Another advantage is that 2-fluid nozzles tend to get blocked less in spray drying processes.

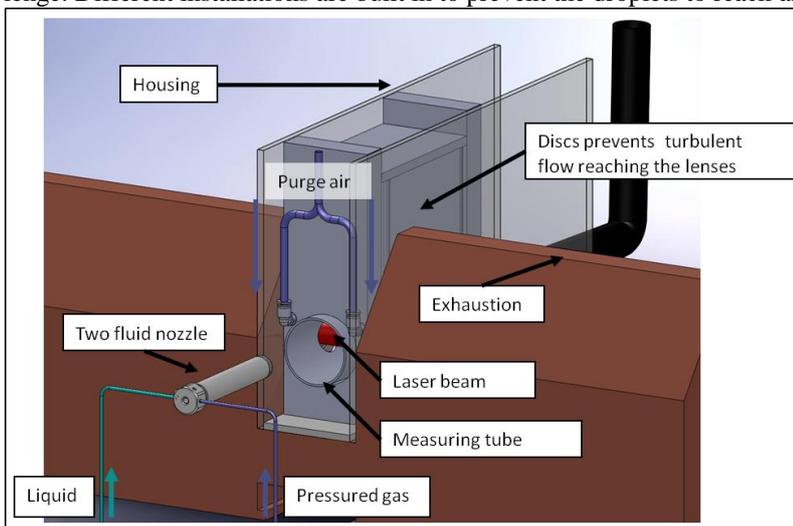
### Measuring the atomization behavior

The droplet formation during the atomization is dependent on the spraying parameters and the properties of the liquid. Semi empirical equations are developed to calculate a median or Sauter mean diameter  $d_{32}$  of the droplet size distribution (DSD) for different atomizers. For a 2-fluid nozzle the following equation (1) is applicable [3].

$$\frac{d_{32}}{D} = C_3 \cdot \left( \frac{\Delta p_G}{(1+\mu_p)^2} \right)^m \cdot (1 + C_4 Oh^j) \quad (1)$$

Different empirical constants like  $C_3$ ,  $C_4$ ,  $m$  and  $j$  show that the atomization is complex. Wide measurements are necessary to fit the constants in order to describe the droplet size for a given nozzle mathematically. Thus a study of atomizing polymer solutions is done first to get information about the droplet formation of such solutions.

These measurements are done with different water soluble polyvinylpyrrolidone (PVP) of different molecule weights. A measuring device for the determination of the DSD is build and illustrated in figure 1. The DSD is measured by laser diffraction and analyzed with Fraunhofer diffraction equation. The knowledge of the optical properties of the spray is not necessary. The device is HELOS<sup>®</sup> by Sympatec with a measuring range from 0.5–175  $\mu\text{m}$ . The measuring of fine droplets in the range of 10 microns within a strong turbulent flow is a great challenge. Different installations are built in to prevent the droplets to reach and pollute the optical lenses.



**Figure 1:** Measuring DSD of turbulent flow with fine dispersed droplets

The first installation is a measuring tube (inner diameter 71 mm) that cuts the spray cone. Only droplets passing the tube get measured. This lack of information has to be considered, but consequently no big influence of the results has been recognized. The measuring tube is stacked outside the tube with parallel discs that work as flow straightener and have a hole (diameter 40 mm) as well as the tube in the position of the laser beam, so the installations don't influence the detected diffraction. An additional purge air stream through the parallel discs and an aspiration of the measuring tube are installed as well. The horizontal distance between the tip of the 2-fluid nozzle and the center of the laser beam is 10 cm. The vertical position is the center of the beam.

Without the installations no reliable or reproducible measurement can be obtained. Another advantage of the installations is the optical concentration during the measurement which is in the range of the specification of the device all the time.

All measurements are done with a 2-fluid nozzle where the inner diameter for the liquid is 0.7 mm and the outer for the gas is 1.5 mm. The aspect ratio of the length and diameter of the inner pipe is 4.5. As a model substance water soluble PVP solutions produced by BASF SE of three different molecular weights are used. Luvitec<sup>®</sup> K17 has a mean molecular weight of 9,000 Da, Luvitec<sup>®</sup> K30 49,000 Da and Luvitec<sup>®</sup> K90 1,250,000 Da. In addition to these solutions glycerin-water mixtures of different mass fractions are used to compare the effect of higher viscosities.

### Design of the 3-fluid nozzle

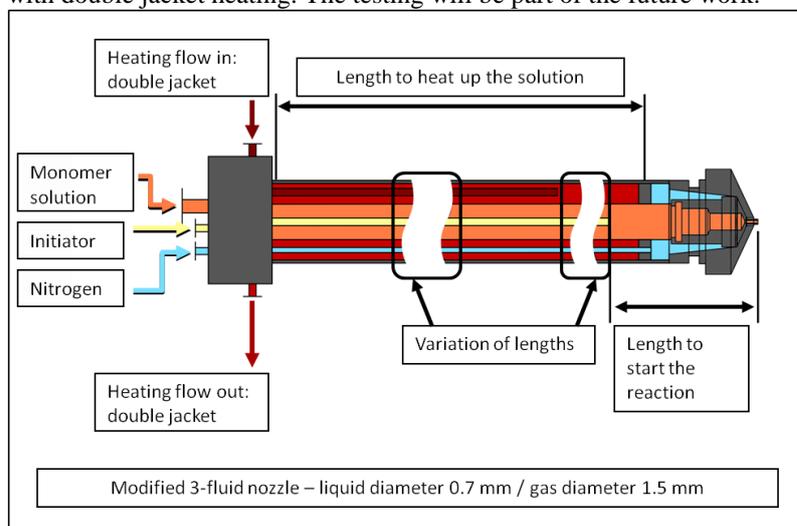
Different types of pneumatic nozzles are available and 3-fluid nozzle has just been patented [4]. The reason for another kind of geometry is that the new designed nozzle has the function to arrange a pretreatment of the reactive monomer solution. The pretreatment should guarantee that the reactive solution is heated up to the desired temperature where a controlled reaction and initiation of the reaction takes place. Because of the use of a thermal initiator the temperature has a high impact on the decomposition rate and defines the starting time.

The geometry of the nozzle is shown in figure 2. Here a double jacket is used to heat up the feed over nearly the whole length of the nozzle. By using a high flow rate of the heating fluid an isothermal process can be ensured.

As it is shown in figure 2 the monomer and initiator solution are centrally fed and mixed internally before the outlet. Here two variations are applied. The variation of the whole length of the nozzle can influence the retention time of the two liquids in the nozzle at a constant flow rate. A constant flow rate is set in order to have no effect on the atomization later on. The second variation is the length of the pipe of the initiator. It varies the place where monomer and initiator get mixed and the polymerization gets started. Finally these variations in geometry of the nozzle are necessary to find an optimum geometry where on one hand the liquids are heated up and on the other hand the reaction's progress doesn't hinder a perfect atomization. If the reaction within the nozzle progresses too far the degree of the polymerization will be high, which affects the viscosity of the liquid, and blocking of the nozzle will occur.

The third fluid is nitrogen at a high pressure, which is fed through the double jacket and finally concentrically to the tip of the nozzle. The nitrogen will expand outside the nozzle and is used to atomize the liquid due to its high velocity. Here nitrogen is used instead of pressured gas because oxygen inhibits the forming of radicals.

At last this 3-fluid nozzle is a combination of a 2-fluid internal mixing and a 2-fluid external mixing nozzle with double jacket heating. The testing will be part of the future work.



**Figure 2:** Modified 3-fluid nozzle with varied lengths to influence the initiator and reaction kinetics before the atomization

But for getting information about the kinetics of the polymerization and the related effect on the atomization a modified measurement has been applied and will be presented in the following chapter.

### Measuring the effect of rheokinetics on a radical polymerization of acrylic acid and its acrylates

The radical polymerization can be generally described in three different steps; initiation, propagation and termination. Normally the monomers are inactive. An initiator becomes decomposed and activates the monomers so that the polymerization gets started. The radicalized monomer starts to form a polymer chain with other monomers. This step is called propagation as the polymer chains grow. The propagation of a polymer chain will be interrupted by inactive polymer chains or monomers or will be terminated by a connection between two active polymer chains. The last step is consequently the termination step.

The radical polymerization is complex and the reaction is described by the help of statistic values, like the distribution or mean value of the molecular weight. One way to characterize a polymerization product is to measure the mean molecular weight by static light scattering or by the intrinsic viscosity also called limiting viscosity number. The intrinsic viscosity will be measured in dilute polymer solutions and is a reciprocal concentration which can determine the mean molecular weight.

The relationship of the molecular weight of a polymer and the viscosity of a polymer in solution is given. Kulichikhin et al. present a theoretical expression (see equation 2) and therefore an analytical method to describe the rheokinetics of a free-radical polymerization [5].

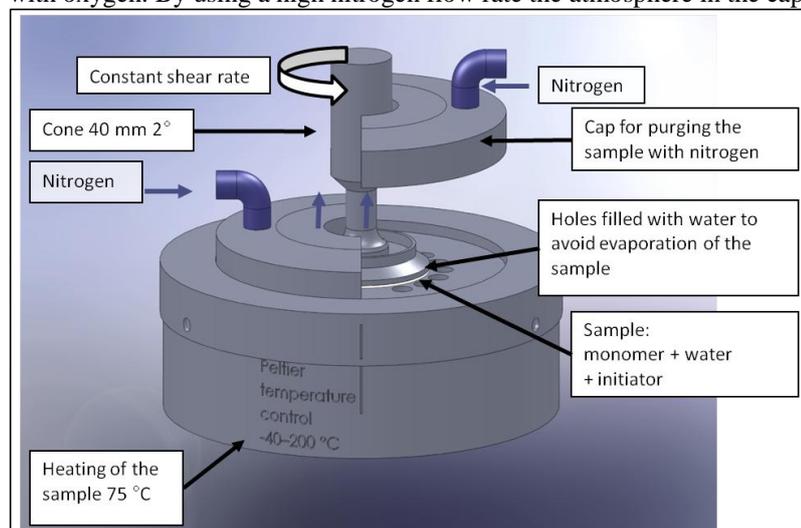
$$\eta = KC^b \bar{M}^a \quad (2)$$

The viscosity  $\eta$  is described with: an empirical factor  $K$ ,  $b$  and  $a$  as determining constants, the mean molecular weight  $\bar{M}$  and the concentration  $C$  of the newly formed polymer.

The idea of measuring the effect of the rheokinetics and therefore describe the kinetics of the polymerization was the motivation for modifying a rheometer as it is seen in figure 3. The standard rheometer has a cone-plate geometry that consists of a cone that is connected to a motor and a plate that is coupled with a peltier temperature control. The rheometer is a HR-1 by TA Instruments with a 2° cone and a diameter of 40 mm. The peltier element controls a temperature between -40 and 200 °C with a controlled heating rate of up to 20°C/min.

For measuring the effect of rheokinetics the rheometer is modified with two semi caps which have a connection to a nitrogen gas flow. So the nitrogen is forced to flow in the caps over the sample and the cone through a small gap to the outside. The gap between the caps and the cone avoids the contact with the cone and any influence on the measured torque. The other modification is an additional plate which fits on the peltier plate and is locked with screws. This plate fixes the cups and avoids evaporation of the sample during the measurement because it has several holes arranged in a circle around the upper cone. If the holes are filled with water, it saturates the nitrogen and creates a saturated atmosphere around the sample.

To get the time dependence of the viscosity at a constant shear rate during the polymerization the following procedure has to be done. First the sample, consisting of the monomer, solvent and the initiator, has to be applied between the cone and the plate. Here a volume of around 585  $\mu\text{L}$  of liquid is necessary. Because of the low sample volume a damage of the rheometer during the exothermic reaction is unlikely. After filling all holes with water the temperature will be increased to reaction temperature as soon as possible. When reaching this temperature the nitrogen gas is turned on and initiates the start of the polymerization. Nitrogen can work as an initiator here because normally the monomers are mixed with inhibitors that avoid the forming of radicals in combination with oxygen. By using a high nitrogen flow rate the atmosphere in the caps is nearly oxygen free in few seconds.



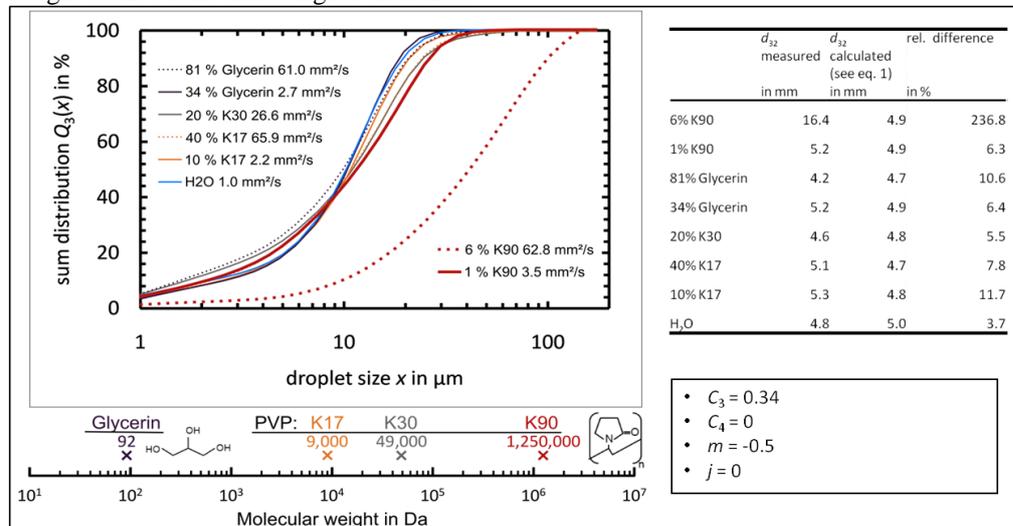
**Figure 3:** Measuring the viscosity under constant shear rate during polymerization in a rheometer

**Results of measured DSDs**

The presented measurements are carried out at one atomization setting with one 2-fluid nozzle as described before. The nozzle is feed with an eccentric screw pump to avoid pulsations of the liquid flow. The gas flow is controlled with a mass flow controller and set to 1346 NL/h. The liquid flow is nearly constant at a rate of 0.1 g/s, so that the gas capacity is 0.22. In order to analyze the influence of molecular weight and viscosity of different water soluble solutions a set of samples are made with similar range of viscosity but different weight fractions. All viscosities are measured with Ubbelohde capillary viscometers. Because of the different capillaries and flow regime the shear rate differs between 1036 and 59 1/s. In this range no non-Newtonian behavior occurs.

The results of the measured DSDs are illustrated in the diagram in figure 4. Each distribution shows mean values of minimal 6 reproducible measurements. It can be recognized that with increasing kinematic viscosity from 1.0 up to 65.9 mm<sup>2</sup>/s all curves of glycerin, PVP K17 and K30 solved in water show nearly the same results. This is supported by the comparison of the measured mean Sauter diameter  $d_{32}$  in the table of figure 4. The difference between the  $d_{32}$  is maximal 1.1 μm. The 1% K90 solution also fits in this range of these Sauter diameters. Based on equation 1 the constant parameters  $C_3$ ,  $C_4$ ,  $m$  and  $j$  were investigated by mathematical iterations. Here the relative difference between measured and calculated values was minimized. The results are shown in the box under the table in figure 4. The iteration shows that in view of these measurements the viscosity seems to be negligible because  $C_4$  is zero and the term of  $Oh$  is also zero.

But compared to the DSD of K90 an effect with increasing viscosity seems to occur. The solution of 6 % K90 generates a measured DSD that is totally different to the other measured curves. If viscosity should have a negligible influence on the droplet formation there is only one property differs K90 from the other solutions. That's the molecular weight as it is also illustrated in a scale under the diagram of figure 4. The molecular weight of K90 is 25 times higher than K30.



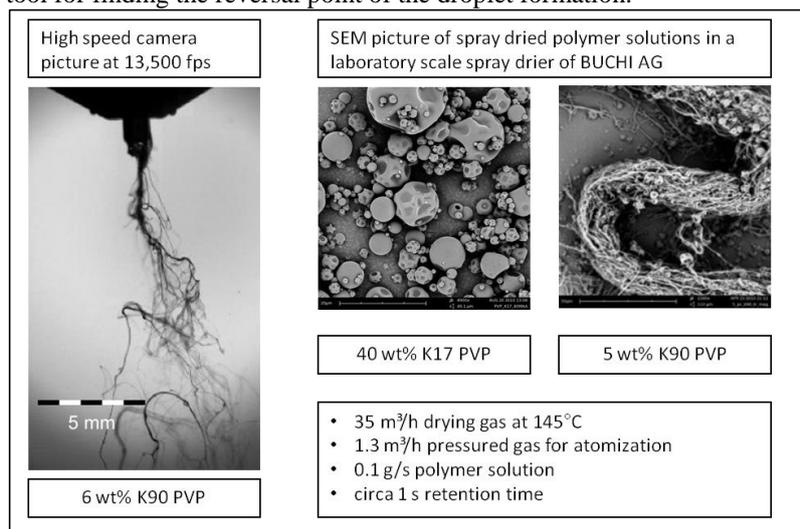
**Figure 4:** Measured DSD of different water soluble molecules of different molecule weight

The influence of molecular weight on the measured DSD can be established by the results shown in figure 5. In the left is a high speed camera picture shot at 13,500 fps. It shows that the 6 % K90 solution forms filaments instead of droplets even in far distance to the nozzle tip which is not typical for 2-fluid nozzles. Normally in the near of the outlet of the nozzle droplets are formed because the high velocity gas impacts the liquid. In addition two SEM pictures are shown in the right of figure 5. These pictures show products of PVP solutions dried in a laboratory scale drier of BUCHI AG. The spray drying was processed under the same atomization settings but with the use of a drying gas at 145 °C and a gas flow at 35m<sup>3</sup>/h. The same result compared to the high speed camera picture can be recognized. Instead of forming droplets that form spherical particles during drying the 5 % PVP K90 solution forms filaments although a higher viscous PVP K17 solution forms particles.

The reason for the different DSD of a 6 % PVP K90 solution is that the atomization generates filaments instead of droplets. The analyzing of filaments with laser diffraction is critical because the diffraction patters are totally different and not symmetrical compared to spheres. A calculated DSD based on these diffraction patters is far away from the truth. Consequently this produces no droplet distribution, but an effect based on the calculation and measuring technique.

Finally it can be defined that with increasing mass fraction a reversal point occurs where polymer solutions of higher molecular mass form filaments instead of droplets or spherical particles eventually. This is the limitation of spraying polymer solution because normally filaments aren't favored. By the knowledge of the behavior

of a certain polymer solution and the effect that filaments produce on the measuring of DSD by laser diffraction is a tool for finding the reversal point of the droplet formation.



**Figure 5:** Comparison of droplet and particle formation between a low and high molecular weight polymer

But the reason for the filament forming hasn't been established yet. As in the literature discussed polymer solutions have a complex rheology and show viscoelastic behavior. The viscoelasticity is strongly dependent on the molecular weight of the polymer [6]. In extensional flows the elastic polymer coils extend and absorb energy during the formation [7]. The energy absorption at a certain strain rate can be measured in extensional rheometers. Newtonian fluids have a Trouton ratio of 3, which is the ratio of extensional to shear viscosity. In polymer solutions non-Newtonian behavior occurs and the Trouton ratio increases dramatically [8]. This is often called as strain hardening and results in bead-on-string structure [9]. An impression of this structure is also present in the SEM picture of a 5 % PVP K90 solution in figure 5. A conclusive proof of this rheological behavior for PVP solutions is still in work and cannot be presented here.

The knowledge of the negative consequences on the atomization of polymer solutions is important when studying the rheokinetics of a radical polymerization of another polymer – poly acrylic acid. To optimize the pretreatment of the reaction within the nozzle the reversal point of the droplet formation is the absolute limit of the propagation. In the following chapter the first results of the effect of rheokinetics are presented and discussed.

### Results of the effect on rheokinetics of the radical polymerization of acrylic acid

Acrylic acid is a very fast reactive monomer with high reaction enthalpy as described before. But the advantage is that a polymerization during a spraying process with a low retention time is successful [2]. The used acrylic acid in this work is applied by BASF SE. For safety reasons it contains an inhibitor like hydroquinone monomethyl ether (MEHQ) which works in connection with oxygen so that no radicals of the acrylic acid will be generated. But by using nitrogen the force of the inhibitor decreases.

The following results describe the time dependency of the viscosity  $\eta(t)$  at a constant shear rate of 300 1/s. Two different mass fraction of solved acrylic acid in water at two different molar fraction of the initiator are shown in figure 6. The experiments are done at a temperature of 75°C and a nitrogen gas flow of 0.1 L/min. All curves show mean values of minimal three reproducible experiments. This accuracy can be visible as all curves show the same plateau at the beginning of the measurement. The plateau is at 0.47 mPa·s and really exact compared to 0.38 mPa·s of water at 75 °C. Different results can be recognized. First the increase of the initiator concentration minimizes the starting point of the polymerization. The starting point can be easily determined as the jump of the viscosity function. In addition a faster start will occur the higher the mass fraction of the acrylic acid is.

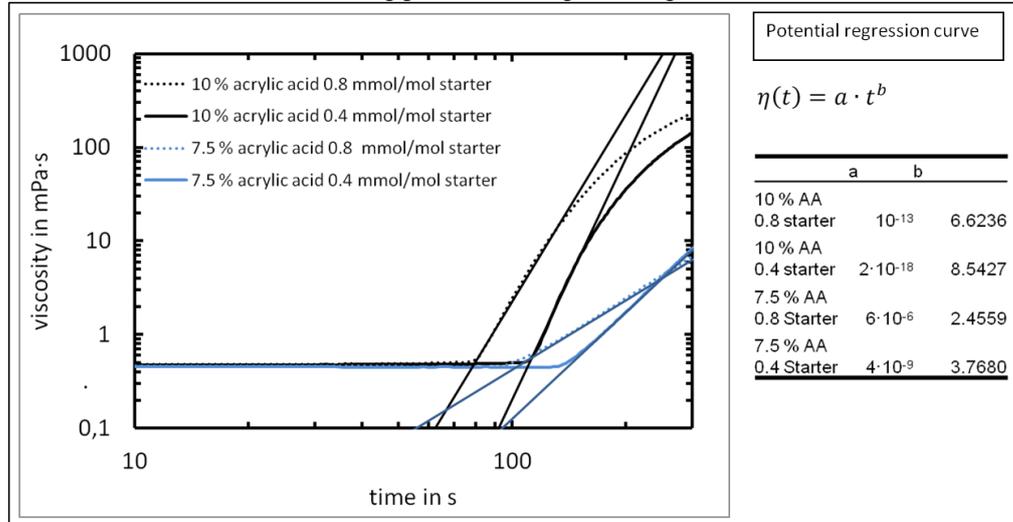
Finally a higher initiator concentration in combination with a higher mass fraction of the acrylic acid increase the gradient of the viscosity function but results in a lower final viscosity. The gradient of the function is illustrated in the right of figure 6. The jump of the viscosity is at first a potential dependency between viscosity and reaction time. By increasing the amount of samples it will generate an empirical description of the effect of rheokinetics by the presented measuring technique.

The aspiring target of this method is to generate semi empirical description as it is presented by Kulichikhin et al. He describes the rheokinetics of polymerization for the initial stage of the process in equation 3 based on equation 2.

$$\eta(t) = K' M_0^a I_0^{b-a} \left( k_p \sqrt{\frac{k_i}{k_t}} \right)^{a+b} t^b \quad (3)$$

Here  $k_p$ ,  $k_i$  and  $k_t$  are the temperature dependencies of the processes of propagation, initiation and termination and  $M$  and  $I$  are the monomer and initiator starting concentrations. Then  $K'$  is the temperature dependence of viscosity and also calculated with an Arrhenius equation.

These measurements are the starting point for testing the design of the 3-fluid nozzle.



**Figure 6:** Measuring the rheokinetics during polymerization of acrylic acid at different concentrations

### Summary and Outlook

The presented work shows the influence of the molecular weight on the atomization of polymer solutions. A reversal point of the droplet formation concerning sprays has been detected by laser diffraction. Established on the rheological behavior of polymer solutions with higher molecular masses stable filaments are formed in the spray. It is suggested that the viscoelastic property of the solution generate high extensional viscosity due to high strain rates during the atomization. Consequently the destruction of the filaments will be avoided.

This is an important result for the polymerization in a spray within a common spray dryer. Here the short retention time will require a pretreatment of the reactive liquid if an efficient process and high yields are proposed. The reversal point is the limitation of the propagation of the polymer chain within the nozzle. By the help of a modified rheometer the viscosity dependent on time is measured. The first results show that the gradient of the initial viscosity jump is empirically expressed by a potential equation.

Detailed research of the rheokinetics is necessary to design a 3-fluid nozzle with an optimal pretreatment. The concept of the 3-fluid nozzle is presented and discussed. Consequently a future work is the testing of the 3-fluid nozzle in a spray dryer. Whether an efficient one step progress is applicable will be demonstrated not till then.

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