

Shear viscosity of fast-reacting aqueous polymer solutions

Magnus Tewes and Urs Alexander Peuker

A power-law function is used in a simple empirical approach to describe the shear viscosity of acrylic acid in water during polymerization.

Quantifying rapid increases in viscosity during polymerization is necessary when designing reaction processes that are sensitive to such changes. Heat and mass transfer in a common reactor are strongly affected by viscosity. A deeper insight into the viscosity function is important for increasing the efficiency of the process, but the simultaneous measurement of viscosity and reaction kinetics is unusual. Furthermore, rheological measurements are performed in a defined narrow gap (50 μm –1mm), and chemically analyzing the material composition within this gap is difficult (especially at high temporal resolution).

In 1996, an in-depth report of a measurement technique aimed at simultaneously characterizing both the rheology (changes in viscosity) and kinetics of a given polymer reaction was published.¹ In this new approach—known as rheokinetics—a viscosity function is calculated, based on reaction kinetics from the literature and empirical parameters determined from measurements of the solution rheology and composition. The advantage of this model is that it provides new possibilities with regard to scaling-up the reaction, but the model is also complex. A measured viscosity function can also be used to predict unknown kinetics. Indeed, this technique has previously been applied to acrylamide polymerization in water.²

We recently reported a simple equation that is based on a power-law function, which can be used to describe the viscosity function of a reacting polymer solution from known kinetics, and we have used this approach to examine the polymerization of acrylic acid in water.³ Like acrylamide polymerization in water, the acrylic acid reaction is a radical (i.e., exothermic) polymerization, but acrylic acid has a higher reactivity (especially at a temperature of 70°C). Acrylic acid is a widely used monomer in the plastics industry, in particular for forming super-absorbing polymers. The focus of our research is the initial stage of polymerization, when the interactions between the molecules are not as complex as at a higher conversion of monomer to polymer.

A sensitive rheometer is an accurate device for determining the changing viscosity of solutions. For example, a cone-plate rheometer

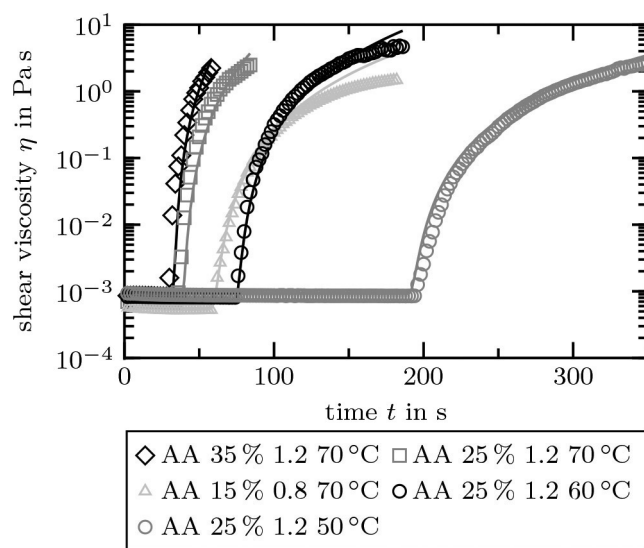


Figure 1. Viscosity function of acrylic acid (AA) over time at different initiator ratios and temperatures. Symbols mark the measured values, and solid lines represent calculations made using our empirical approach.

has been used in the past to measure the complex viscosity during bulk polymerization under oscillation.⁴ For our study, we chose a rotational mode at a constant shear rate. Although this mode provides less information than the oscillating mode, the higher temporal resolution of the rotational mode is advantageous for measuring fast reactions with rapid changes in viscosity. Another setup has been published by Chevrel and co-workers,⁵ who also measured aqueous acrylic acid polymerization using a rotational rheometer, but with a custom-made geometry similar to a stirring vessel. To measure the viscosity of our solutions, we used a DHR-1 cone-plate rheometer from TA Instruments. We modified the device by covering the sample between the cone and plate, and by purging with nitrogen around the sample to avoid reaction with oxygen (oxygen will react with the free radicals and can work as an inhibitor). Our reactive solutions contained acrylic acid (from Sigma Aldrich) and

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deionized water in different mass fractions. We stabilized the acrylic acid with about 200ppm of 4-methoxyphenol (MEHQ). We also added a thermal azo initiator, V-50 (Wako Chemicals), which has an initiator ratio of 0.8 and 1.2mmol/mol relative to moles of acrylic acid.

In Kulichikhin and Malkin's² rheokinetic model, the viscosity function $\eta(t)$ —where t is time—is determined by a power-law function. We adopted their theory, but we modified the equation using a dimensionless form. Our equation is therefore calculable at the beginning of the reaction, i.e., when $t = 0$.³ By assuming isothermal conditions and reaction coefficients independent of acrylic acid concentration, we derived a simplified function to describe the specific viscosity (η_{spec}) over t :

$$\eta_{\text{spec}} = \frac{\eta(t) - \eta_{\tau}}{\eta_{\tau}} = \alpha \cdot t_{\text{red}}^b \quad (1)$$

Here the viscosity function is dependent on t_{red} , which is the measured time reduced by the induction period (τ). The empirical parameters α and b determine the power-law function, where α differs with temperature and composition according to the theory of Kulichikhin and Malkin.² The induction period of the polymerization occurs at the beginning of the measurement and exhibits a viscosity plateau with passing time (see Figure 1). During this period, the radicals that are freed by the decomposition of the initiator react with the inhibitor system (i.e., dissolved MEHQ) and oxygen. After one component—MEHQ or oxygen—is consumed, acrylic acid begins to polymerize. The induction period depends strongly on the initiator concentration,³ i.e., the higher the initiator concentration, the greater the number of free radicals in the solution. The higher number of radicals reacting with the inhibitor system will thus ultimately shorten the induction period. The viscosity, η_{τ} , is the shear viscosity after the induction period, and the specific viscosity, η_{spec} , is the dimensionless form.

The measured viscosity function of acrylic acid at different initiator ratios (0.8 and 1.2mmol/mol), temperatures (70, 60, and 50°C), and mass fractions (35, 25, and 15%) is shown in Figure 1. All these results indicate a large increase in viscosity after passing the plateau or induction period. In addition, the influence of the mass fraction of acrylic acid and temperature is apparent. The lower the mass fraction (concentration), the lower the gradient of the viscosity. The same influence is shown with lower temperatures, as described by Arrhenius's law. In contrast to the gradient, we find that the induction period is strongly affected by the lower temperatures, i.e., the induction period is enlarged by a factor of four as the temperature decreases from 70 to 50°C. The solid lines in Figure 1 show the viscosity calculations based on our empirical approach (see Equation 1). As the temperature is decreased from 70 to 60 to 50°C, the average exponent b decreases from 2.6 to 2.5 to 2.3.

A comparison of all our results shows that b varies with the concentration of acrylic acid,³ which is contrary to the findings of Kulichikhin and Malkin.² We found that b increases significantly when the initial

concentration of acrylic acid is also increased. A constant b therefore cannot be assumed over the broad range of variations. In addition, we analyzed the pre-exponential factor (α), which combines the different reaction coefficients and concentrations. Here we used the kinetics of acrylic acid polymerization.^{6,7} Calculations of the pre-exponential factor from the theory of Kulichikhin and Malkin² are in good agreement with our analyzed pre-exponential factor α . We did not find any additional dependencies of α that are contrary to the established theory, but we have analyzed empirical parameters that are not of the same magnitude as those of Kulichikhin and Malkin.²

In summary, we have introduced an empirical viscosity function for characterizing the initial state of the polymerization of acrylic acid over time. We conclude that, when dealing with fast reactive systems, measuring viscosity is a quick way to measure changes. Our approach is successful even though the viscosity of a polymer solution is a mechanical property that describes the fluid's resistance to deformation. In future work, we plan to refine the rheokinetic approach to better understand why our results differ from the previously published reports. We also need to devise an additional method for simultaneously analyzing both the kinetics and rheology of the reaction. If the polymer concentration or the conversion of monomer and the molecular weight of the polymer can be determined at different times in the rheometer, the empirical approach can be further extended to a rheokinetic approach. This means that the 'kinetic' part of the rheokinetic approach will no longer be based only on literature values. We have conducted initial tests to determine a viscosity function that is dependent on time and on the measured conversion of monomer to polymer. A detailed understanding will help to extend the theory of rheokinetics.

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Author Information

Magnus Tewes and Urs Alexander Peuker

Technische Universität Bergakademie Freiberg
Freiberg, Germany

Magnus Tewes is a PhD candidate. His research activity focuses on the study of the rheokinetics of acrylic acid polymerization in water, and its application in a novel process known as polymerization in sprays.

Urs Alexander Peuker is a full professor of mechanical process engineering and mineral processing. His research activity is focused on particle technology, recycling processes, and filtration applications.

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