Online Rheo-TD NMR for analysing batch polymerisation processes

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ABSTRACT

A compact low-field NMR rheometer has been developed for process analysis by means of rheometry and NMR relaxometry. On the basis of an NMR capillary rheometer for close to ambient conditions, a flow-through system with an inductively coupled probe head for elevated temperatures (up to 423 K) and pressures (2 MPa) was realised.

A fast measurement of the Abel transform of the velocity-dependent phase factor in the capillary is performed using a 2-axes-gradient system. Assuming Ostwald-de Waele or Hershel–Bulkley behaviour the power law index and (if applicable) the rheological yield point is extracted. Values are validated against data from a rotational viscosimeter.

During polymerisation the increasing solid content provides information about the progress of reaction while the interaction between the polymer and the water phase manifests itself via the relaxation time of the water phase. Both parameters can be determined from a solid echo followed by a CPMG train.

NMR relaxometry on flowing samples of solutions and dispersions is confronted with complex effects as spatially dependent excitation and detection efficiency and incomplete polarisation especially for slow relaxing liquids. A theoretical description of the effects is developed and used for a correction of the magnetisation decay curves. It requires knowledge of the velocity probability density function which is known if the flow profile has been determined. In order to reduce incomplete polarisation effects, a prepolarizer using specially designed Halbach magnets is used.

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1. Introduction

Batch polymerisation processes are often monitored and controlled via only a few parameters such as pressure, temperature and stirring power. Additional information from novel analytic methods may provide a basis for a better understanding of these processes as well as new options for process control and quality assurance.

Viscosity is a key parameter during the various stages of the polymerisation process. In a bypass line it can be measured by capillary rheometry. However, only the effective viscosity for the given flow rate can be established this way. For obtaining the viscosity function, a number of flow rates have to be examined and iterative corrections have to be applied.

Another route to viscosity is given by the evaluation of the velocity profile in the capillary [1,2]. Combined with a pressure drop measurements along the line, the viscosity function for the shear stress range occurring in the capillary can be obtained.

The feasibility of such measurements with low field NMR-equipment has been proved [3,4]. In the current work the set up from [3] has been adapted to the conditions found in polymerisation vessels.

Apart from determination of the viscosity function, NMR is also capable of determining other parameters which provide additional information on the polymerisation process. From the transverse relaxation of the water phase, the interaction between water and polymer can be monitored. Measurement of T_2 relaxation rates under flow was already studied by Singer [5]. Correction of flow impact basically included allowances for mean residence time of the fluid in the measuring volume. This correction is improved by a theoretical description and a numerical implementation of the effects of spatially dependent excitation and detection efficiency [6].

For monitoring the start of polymerisation and its progress, information about the first appearance of solid content and its increase during polymerisation is of major interest. The evaluation of solid echo followed by a CPMG train provides information about this [7]. While the solid echo is hardly influenced by flow effects, the CPMG information needs correction due to flow as studied in the T_2 relaxation experiment.

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2. Experimental

2.1. NMR based capillary rheometry

Depending on the equipment NMR offers various possibilities for measuring velocity profiles. With simpler low field systems with one gradient axis in the flow direction, velocity profile is determined by analysis of the velocity probability density function. The velocity probability density function is determined by means of Fourier transform of a Pulsed Gradient Spin Echo signal with varying encoding steps [1]. However, for satisfying velocity resolution many encoding steps are required and experimental times often exceed half an hour depending on relaxation behaviour of the fluid. Online monitoring of processes needs faster approaches.

NMR equipment with 3 gradient axes allows to determine the velocity profile by imaging sequences directly in a thin slice using e.g. FEVI [8]. However, this decreases the signal to noise ratio, making the applicability in low-field bench top devices difficult.

Considerably faster encoding of the velocity dependent phase factor with adequate signal noise ratio is possible by using an NMR system with 2 gradients. When using one axis for spatial resolution and one for the measurement of the velocity dependent phase shift, the Abel transform of the phase shift can be measured with only a few encoding steps. Assuming radial symmetry which is true for fully developed laminar flow in circular pipes, the velocity profile can be calculated using a discrete inverse Abel transformation [9,10].

As the inverse Abel transform is very sensitive to noise a different approach is chosen to evaluate the measurements gained with the compact 10 MHz system. The magnetisation M^+ of an ideal experiment in the $(k, \tilde{q})$-space reads

$$M^+(k_x, \tilde{q}_y) = l_y \rho_0 \int_0^{2\pi} \mathrm{d}\varphi \int_0^R r \mathrm{d}r \cdot \exp(ik_x r \cos \varphi) \cdot \exp(i\tilde{q}_y v(r)) \tag{1}$$

with l_y representing the length of the radio frequency (RF) field, ρ_0 the spin density, φ the azimuth angle, R the maximal radius of the observed area and r the radial coordinate. Assuming a parameterized function for the velocity profile $v(r)$, its parameters can be determined by a fit of the signal calculated by Eq. (1) to the measured signal. Before fitting the expression in Eq. (1) and the measured signal both are Fourier transformed in k space. The φ-integral can be calculated analytically leading to a Bessel function. The velocity profiles are chosen according to Ostwald-de-Waele $\tau = k(-\frac{\mathrm{d}v}{\mathrm{d}r})^n$ or Hershel–Bulkley behaviour $\tau = k(-\frac{\mathrm{d}v}{\mathrm{d}r})^n + \tau_0$. They can be expressed as follows:

Ostwald-de-Waele fluid with exponent n:

$$v(r) = \frac{3n+1}{n+1} v_{\mathrm{mean}} \left(1 - \left(\frac{r}{R}\right)^{\frac{n+1}{n}}\right) \tag{2}$$

Hershel Bulkley fluid with exponent n and r_0 representing the radius of the inner cylinder with plug flow due to yield stress τ_0:
for $0 < r < r_0$

$$v(r) = v_{\mathrm{max}} \tag{3}$$

$$= v_{\mathrm{mean}} \left(\frac{n+1}{3n+1} + \frac{2r_0 n(n+1)}{R(3n+1)(2n+1)} + \frac{2n^2 r_0^2}{R^2(3n+1)(2n+1)}\right)^{-1}$$

for $r_0 < r < R$

$$v(r) = v_{\mathrm{max}} \left(1 - \left(\frac{r - r_0}{R - r_0}\right)^{\frac{n+1}{n}}\right) \tag{4}$$

with mean velocity v_{mean} calculated from the flow rate set in the experiment. Expressing the maximum velocity in Eq. (4) by the mean velocity reduces the number of fit parameters by one.

As the plug flow radius r_0 is dependent on the actual flow rate it has to be expressed by the yield stress in order to fit experimental results at different flow rates simultaneously. In this situation the velocity profile is expressed as:
for $0 < r < x_1/a$

$$v(r) = v_{\mathrm{max}} \tag{5}$$

$$= v_{\mathrm{mean}} \left(1 - \frac{2}{a(x_2 + 2)} \frac{aR - x_1}{R} + \frac{2}{a^2(x_2 + 2)(x_2 + 3)} \left(\frac{aR - x_1}{R}\right)^2\right)^{-1}$$

for $x_1/a < r < R$

$$v(r) = v_{\mathrm{max}} \left(1 - \left(\frac{ar - x_1}{aR - x_1}\right)^{x_2 + 2}\right) \tag{6}$$

with fit variables

$$x_1 = \frac{\tau_0}{k} \tag{7}$$

$$x_2 = \frac{1}{n} \tag{8}$$

and parameter

$$a = \frac{\Delta p}{2Lk} \tag{9}$$

Δp is the pressure difference along the flow path at the distance L. The factor k represents the flow consistency of the medium.

The previous integration limit r_0 can be calculated using $r_0 = x_1/a$. If the pressure difference Δp is not being measured, the variable a at each flow rate can be determined for each set of x_1 and x_2 by numerical solution of the implicit equation

$$2\pi R^2 v_{\mathrm{mean}} = \frac{(aR - x_1)^{x_2 + 1}}{a(x_2 + 1)} \left(\pi R^2 - \frac{2\pi}{a(x_2 + 2)}(aR - x_1)R + \left(\frac{2\pi}{a^2(x_2 + 2)(x_2 + 3)}\right)(aR - x_1)^2\right) \tag{10}$$

Eq. (10) expresses the flow rate by the analytical integral of Eqs. (5) and (6).

In our measurement dead time was 12.5 μs. Eight steady state pulses on the PGSE gradient are executed before the PGSE sequence starts in order to eliminate problems with eddy currents and magnetic memory effects in the permanent magnet [11]. In order to avoid eddy currents a constant read gradient is applied throughout the sequence. The four possible combinations of read and PGSE gradient polarities are used in the averaged signal, taking into account the reversal of the spatial axis (read gradient) and the change in sign of the velocity dependent phase (PGSE gradient), see k and $\tilde{q}$ in Eq. (1). For each gradient combination 12 scans were averaged. Overall experimental time is approximately 5 min depending on relaxation rates of the sample.

2.2. Solid content determination and NMR T_2 relaxometry

A combined measurement of solid echo and T_2 relaxation for determing the solid content in a sample has been introduced by Maus et al. [7] using a sequence $(90)_x - \tau_s - (90)_y - \tau_s - (acq) - \tau_{cpmg} - [(180)_y - \tau_{cpmg} - (acq) - \tau_{cpmg}]_n$. In our experiment parameters were set to τ_s = 12.5 μs, τ_{cpmg} = 120 μs and n = 4096.

Due to the demand of continuous flow in the bypass, the magentisation decay curves are measured in the flowing sample. This has to be regarded in two ways. For slow relaxing fluids, the permanent magnet may not be sufficient for complete polarisation of the sample. In addition to this, spatial inhomogeniety of the RF field will lead to a change in measured values from flowing samples compared to static samples.