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Hydrodynamic Activation of the Batch-Polymerization of Methyl methacrylate in a Taylor-Couette Reactor

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Summary: In this work, the free radical batch polymerization of methyl methacrylate (MMA) premixed with xylene as a solvent, in the presence of an initiator, 2,2-azoisobutyronitrile (AIBN), in the Taylor-Couette reactor was studied. We observed an unexpected influence of hydrodynamic process parameters, i.e. angular velocity ω, on the polymer conversion, molecular weight and viscosity of the produced polymer. The polymerization process seems to be activated by hydrodynamic process parameters. Hydrodynamic activation is a promoting effect of process parameters on polymer product properties. The hydrodynamic activation is found to depend on the reaction time and the angular velocity of the inner cylinder. In addition, our results highlight both the reaction kinetics and the hydrodynamics during the polymerization. The conversion exhibits a significant difference between tests with and without the angular velocity of the inner cylinder. The conversion and the molecular weight strongly increase with the increase of the angular velocity of the inner cylinder, whereas the viscosity is less strongly dependent. There is more increase with decreasing solvent concentration. The radial Reynolds number decreases with increasing conversion. The polymerization is faster with a low solvent concentration, and the molecular weight is higher compared to the case of high solvent concentration.

Keywords: batch polymerization; hydrodynamic activation; methyl methacrylate (MMA); solution polymerization; Taylor-Couette reactor

Introduction

A Taylor-Couette reactor (TCR) consists of two concentric cylinders of which the inner cylinder is rotating and the outer one is at rest. The flow induced by the rotation of the inner cylinder, with or without a superimposed axial flow, is characterized by the existence of hydrodynamic instabilities of inertial origin, the basic instability mode consisting of axis-symmetric counter rotating vortex cells (Taylor vortices) spaced regularly along the axial direction, see Figure 1. The TCR provides certain advantages for a number of practical applications.[1]

The free radical polymerization of polymethyl methacrylate (PMMA), for example, exhibits gel, glass and cage effects. During polymerization reaction, the polymer conversion *X* and polymer maximum molecular weight M_w increase rapidly, leading to an increase in viscosity of the reaction medium. While there is a considerable amount of data in the literature for reacting polymer solutions and melts in stirred tank reactors, there is scarcely any information available on polymerization in a Taylor-Couette reactor. Some researchers[3–7] have measured polymer conversion, average molecular weight and viscosity in a stirred tank; ÓNeil, Wisnudel and Torkelson[8,9] studied the free radical polymerization kinetics of MMA

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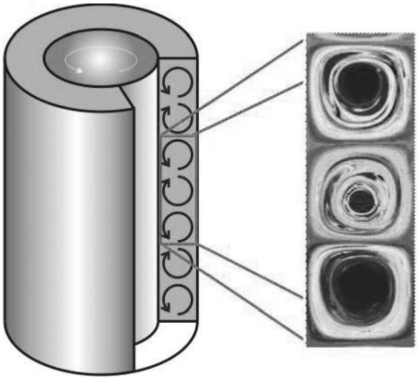

Figure 1.
Taylor-Couette flow featuring the first instability mode.[2]

using tubes in which there is no flow in a constant temperature water bath; Buback, Busch and Beuermann[10–17] have studied the polymerisation kinetics of MMA, especially at high pressures. However, there is no description of the influence of the angular velocity of the stirrer on the product parameters in a stirred tank reactor, and there is also no description of the differences in experimental data between polymerization in a stirred tank and stagnant polymerization in tubes. Sangwai et al.[18] carried out bulk polymerization of MMA in a rotational Couette viscometer under non-isothermal conditions. They measured the viscosity and the temperature as a function of time and developed a correlation relating viscosity to X and M_w for two different initiator loadings. Moritz et al.[19–21] determined the resident time, propagation rate constant k_p and heat transfer coefficient α of N-buthyl methacrylate and stryrene during the emulsion polymerization in a TCR. Again however, they did not investigate the influence of the hydrodynamic process parameter on the product parameters, i.e. conversion, molecular weight and viscosity, or try to determine the transient flow behaviour based on the viscosity rise during reaction. From the literature review, we have not found that the product properties are dependent on the hydrodynamic process parameters. The difference between with and without rotational stirring in a reactor has not been observed. The hydrodynamic activation of a polymerization in a Taylor-Couette reactor has not been reported.

It is the aim, therefore, of this work to find the relationship between hydrodynamic process parameters and product parameters in a specially designed Taylor-Couette reactor using a free radical solution polymerization of MMA (as an example system) at a reaction temperature of 80 °C with AIBN as an initiator. The independent variables considered in this work are angular velocity, solvent concentration and reaction time, while the measured quantities are conversion, molecular weight and shear viscosity wherewith the rotational Reynolds number is calculated.

Set-Up and Data Evaluation

A Taylor-Couette system was used because of its homogeneous energy dissipation. Its performance can be described using the following coefficients: radius ratio

$$\eta = \frac{R_i}{R_i + d} \quad (1)$$

where R_i is the radius of the inner cylinder and d the gap width between the two cylinders, and aspect ratio, which is the length of the fluid column, L, divided by the gap width between the two cylinders,

$$\Gamma = \frac{L}{d} \quad (2)$$

which gives the number of Taylor vortices that occupy the fluid column.

The flow stability in the case of a rotational Taylor-Couette flow with superimposed axial flow can be described by means of two dimensionless numbers: the rotational and axial Reynolds numbers, Re_ϕ Eq. (3) and Re_{ax} Eq. (4),[22]

$$\mathrm{Re}_\phi = \frac{\omega \cdot R_i \cdot d}{\nu} \quad (3)$$

$$\mathrm{Re}_{ax} = \frac{u_{ax} \cdot 2d}{\nu} \quad (4)$$

where ω is the angular velocity of the inner cylinder, and υ is fluid kinematic viscosity. According to the linear stability theory, the critical rotational Reynolds number for different flow regimes can be formulated as a function of the radius ratio,[23]

$$\mathrm{Re}_{\phi,crit} = \frac{\omega_{crit} \cdot R_i \cdot d}{\nu}. \tag{5}$$

$$\mathrm{Re}_{\phi,crit1} = \frac{1}{0.1556^2} \cdot \frac{(1+\eta)^2}{2\eta \cdot \sqrt{(1-\eta)\cdot(3+\eta)}}. \tag{6}$$

The radial Reynolds number decreases with the increase of the viscosity of the reaction medium, and increases with the increase of the angular velocity of the inner cylinder. Thus, based on the main flow regimes observed for the flow of a Newtonian fluid in a reactor replica (see Table 1), the transient flow patterns could be estimated.

The reaction kinetics of the solution polymerization of MMA is assumed to follow the free radical polymerization mechanism presented in Table 2.

In this work, chain transfer reactions to both solvent and monomer have not been considered. The polymerization rate from the above mechanism can be written as[26]

$$-\frac{dc_{monomer}}{dt} = K \cdot c_{monomer} \cdot \sqrt{c_{initiator}} \tag{7}$$

with

$$c_{initiator} = c_{initiator,0} \cdot \exp(-k_d \cdot t) \tag{8}$$

The polymerization rate constant K is a function of decomposition rate constant k_d, propagation rate constant k_p and termination rate constant k_t.[26]

$$K = \frac{k_p}{\sqrt{k_t}} \cdot \sqrt{2f \cdot k_d} \tag{9}$$

in which $k_t = k_{tc} + k_{td}$ (termination rate constant for combination k_{tc} and for disproportionation k_{td}) and f is initiator efficiency. The propagation and termination ratio $k_p/\sqrt{k_t}$ can be defined as follows:[27]

$$k \equiv \frac{k_p}{\sqrt{k_t}} \tag{10}$$

Table 1.
Main regimes in Taylor-Couette flow with inner cylinder rotating and outer cylinder at rest.[24]

critical radial Reynolds number $\mathrm{Re}_{\phi,crit}$	flow regime
< 126	laminar Couette flow (LCF)
126	Taylor vortex flow (TVF)
136	wavy vortex flow (WVF)
> 5036	turbulent Taylor vortices (TTV)

Table 2.
Free radical polymerization main mechanism.[25]

initiation		$I \xrightarrow{k_d} 2R\cdot$
propagation		$M + R\cdot \xrightarrow{k_{p1}} MR\cdot \equiv P_1\cdot$
		$P_n\cdot + M \xrightarrow{k_{pn}} P_{n+1}\cdot$
termination	combination	$P_m\cdot + P_n\cdot \xrightarrow{k_{tc}} P_{m+n}$
	disproportionation	$P_m\cdot + P_n\cdot \xrightarrow{k_{td}} P_m + P_n$

Experimental Set-Up

According to the aim of our work, the experimental set-up allows for the controlled free radical solution polymerization of MMA in a TCR at isothermal conditions. The experimental unit is shown in Figure 2. The TCR consists of two vertical stainless steel cylinders with the length of 390 mm. The inner diameter of the outer cylinder is

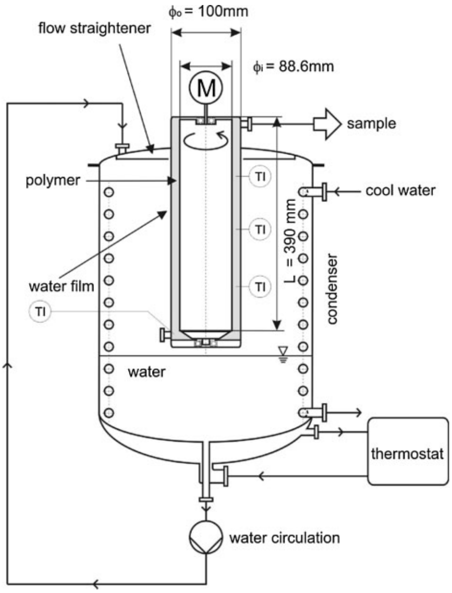

Figure 2.
Taylor-Couette reactor.

100 mm and the outer diameter of the inner cylinder is 88.6 mm, yielding the following geometrical parameters: $\eta = 0.89$, $\Gamma = 68$. Thus, the resulting critical radial Reynolds number in the gap is $Re_{\phi,crit1} = 126$ for the onset of vortices, according to Eq. (5). In the experiments presented in this study, the axial Reynolds number was $Re_{ax} = 0$, meaning there was no axial through-flow. The bottom of the inner cylinder is conical in shape with an angle of 45° to the axis (this means the total length of the cylinder is some 40 mm larger, including the conical part). The outer cylinder is enclosed in an air-free water tank that contains both a heating and cooling system, designed to maintain the temperature constantly in the reactor. The heating system is composed of a water pump situated at the base of the reactor that drives fluid from the bottom to the top of the tank and then through a flow straightener situated in the vicinity of the outer cylinder of the TCR. Thus a thin water film with a thickness of about 5 mm is formed along the outer wall of the outer cylinder that insures a uniform temperature distribution during the polymerization of MMA. The thermostat is used to temper the water film. Cooling capacity is provided by a pipe coil which is placed close to the inner wall of the water tank. The maximum temperature difference between the gap and the water film is calculated in Appendix A. The temperature in the gap deviates from the coolant temperature by no more than $\Delta T_{max.} = 2.5K$.

Experiment

In the present work, the batch polymerization of methyl methacrylate (MMA) at 80 °C under different reaction regimes, such as the solvent concentration and velocity of the inner cylinder, was chosen as a case study to find the relationship between product and process parameters in the TCR. The polymerization reactions were performed with monomer in the 660 ml reactor. The concentration of initiator was 0.02 wt.% in all the experiments. In order to avoid the gel effect and high viscosity of the reaction medium during the reaction, three different solvent (xylene) concentrations (60, 70 and 80 wt.%) were used. The reaction mixture was sampled every 60 min and the solid content was determined by drying off the solvent and the residual monomer.

The extracted samples were mixed with the 2,2,6,6-tetramethylpiperidin-1-oxy (TEMPO) inhibitor in order to stop the polymerization. Afterwards, all the samples were stored at minus 30 °C for conservation. Methyl methacrylate (MMA) was supplied by Merck Schuchardt OHG, xylene isomers by Carl Roth GmbH, and 2,2-azoisobutyronitrile (AIBN) and 2,2,6,6-tetramethylpiperidin-1-oxy (TEMPO) by Sigma-Aldrich. Samples were dried in a vacuum oven at 150 °C for six hours, and weighed for conversion, Eq. (11).[28]

$$X = \frac{w_P}{w_{m0}} = \frac{w_P}{w_{mix} - w_s} \tag{11}$$

where w_P , w_{m0} , w_s and w_{mix} present the weights of the polymer, the initially charged monomers, solvent, and the reaction mixture of a sample, respectively.

Molecular weight characterization was performed by gel permeation chromatography (GPC) using tetrahydrofuran (THF) from Carl Roth GmbH as the solvent and mono disperse PMMA standards by Sigma-Aldrich for calibration. The rheological measurements were performed using a Physica MCR101 rotational rheometer for the reaction temperature, on a cone-plate geometry modified by the addition of a solvent trap to avoid substance evaporation during the steady shear and oscillatory measurements. The zero shear viscosity is defined as the viscosity at the limit of low shear rate.

Results and Discussion

Flow Behaviour During the Polymerization in a TCR

The radial Reynolds number depends on the viscosity of the reaction medium, given that the angular velocity and the geometry are constant. The viscosity of the reaction medium during batch polymerization increases with the reaction time. Thus, the viscosity is the main factor which influences the transient flow behaviour in the reactor. Figure 3 shows the experimental results of the radial Reynolds number for different angular velocities of the inner cylinder and two solvent concentrations. It could be assumed for all solvent concentrations that the flow begins with turbulent Taylor vortices (TTV), and with a decreasing rotational Reynolds number, the flow enters the secondary and primary instability modes, WVF and TVF. In respect of this, different solvent concentrations yielded different results: for 80 wt.% xylene (in Figure 3a), the flow at the end of the reaction is within the wavy regime, while for 60 wt.% xylene (in Figure 3b), it is below the critical rotational Reynolds number, $Re < Re_{\phi,crit1}$, the flow being thus laminar Couette flow (LCF); for 70 wt.% xylene, the terminal flow regime is somewhere around Taylor vortex flow (TVF). The rates of decrease in the rotational Reynolds number also vary with solvent concentrations. For 60 wt.% xylene at all tested ω, the backwards transition from TTV to WVF occurs for $t < 100$ min, while for 80 wt.% xylene, the same transition occurs for $t > 200$ min.

In addition, for 60 wt.%, the spread of transition lines to WVF is rather narrow, occurring for $50 < t < 240$ min, before settling at LCF as the stationary regime. Another influence of the solvent concentration is that of the angular velocity ω, as for 80 wt.% xylene, the results show a significant increase of the Reynolds number with ω in comparison with the lower concentration solutions (compare Figure 3a with 3b). This yields a wider range for transition times at different ω, namely in the range of $200 < t < 350$ min for 80 wt.% xylene, with the longest transition time occurring for the highest angular velocity, $\omega = 66$ rad/s. Therefore, the solvent concentration plays a major role in the hydrodynamics of batch polymerization. The higher solvent concentration hinders the reaction rate, because for the free radicals the probability of meeting a monomer molecule is lowered. In contrast, termination in diluted solutions is faster than in undiluted because of the lowered viscosity. In consequence, using a higher concentration of solvent, the rate of increase in viscosity is reduced during polymerization, and as a result, the radial Reynolds number in the polymerization with 60 wt.% solvent decreases at a higher rate compared to 80 wt.%. On the other hand, the solvent dilutes the polymer solution. Thus, the shear viscosity at the end of the polymerization using 60 wt.% xylene is higher than with 80 wt.%. This is the reason why the flow regime is stabilized in the subcritical region (LCF) for reaction with the 60 wt.% xylene. Flow regimes play

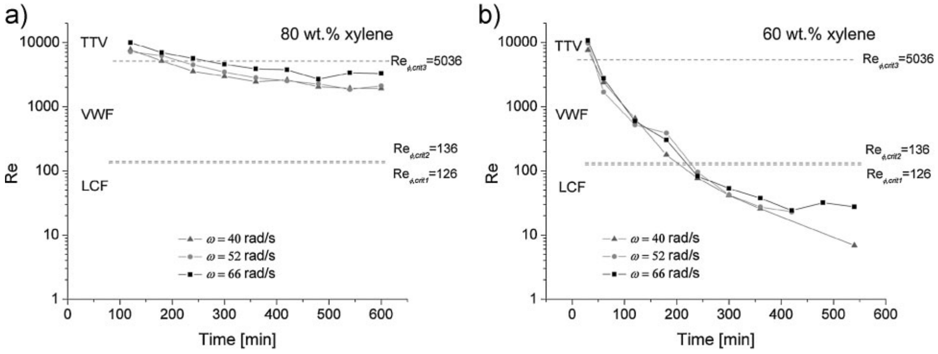

Figure 3.
Experimental data for radial Reynolds number for different rotational speeds of the inner cylinder using two solvent concentrations: a) 80 wt.% and b) 60 wt.% xylene.

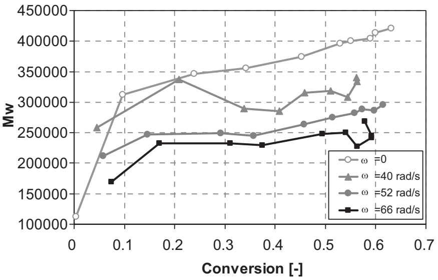

Figure 4.
Molecular weight – Conversion profile for the batch polymerization with 60 wt.% xylene with the different rotational speeds of the inner cylinder.

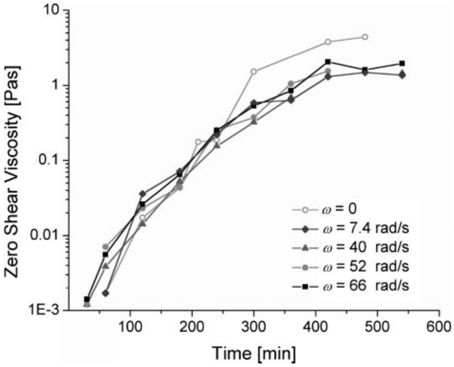

Figure 5.
Zero shear viscosity during the batch polymerization with different rotational speeds of the inner cylinder in the TCR with 60 wt.% xylene.

a major role in the determination of the influence of the mixing on polymerization in the TCR.

Molecular Weight and Zero Shear Viscosity

In this work, a comparison of molecular weights in the batch polymerization with (ω > 0) and without (ω = 0) rotation of the inner cylinder is given in Figure 4 for the 60 wt% xylene case. Thus one can see that there a qualitative difference between the test cases. While poor heat and material transfer in the static TCR (ω = 0), the molecular weight increases significantly with increasing conversion. By simple calculation it can be shown that the maximum temperature difference between the polymerizing mixture in the gap and the cooling water film on the outside of the TCR does not exceed 1 Kelvin. Furthermore, there is no mixing in the reactor. However, the molecular weight in the other cases (ω > 0) is not a function of conversion, being instead almost constant during the polymerization. Moreover, the molecular weights for ω > 0 are quantitatively very close, and increase with increasing ω. The experimental results with 70 and 80 wt.% xylene are similar to 60 wt.%.

The zero shear viscosities of the polymerizing product during batch polymerization with different angular velocities of the inner cylinder are presented in Figure 5. At the beginning of the reaction, there is a weak dependence of the process parameter ω on the zero shear viscosity, while in the case of ω = 0 towards the end of the polymerization viscosity is higher than for the cases with a rotating inner cylinder (ω > 0). At ω > 0 it is expected that the reaction is homogeneous in the reactor domain, with polymerization rates being almost the same. As can be seen in Figure 5, the influence of angular velocity on the zero shear viscosity is minimal for all solvent concentrations (the rotational Reynolds number was computed using the viscosity for the respective shear rate). The explanation for this behaviour relies on the fact that in the absence of ω > 0, as the viscosity of the reaction medium increases, the reaction should be heterogeneous. This would lead to a local acceleration of reaction rate in the domain and thus the viscosity should increase at a higher rate with ω = 0.

Several researchers[29–33] have presented that the melt viscosity of the polymerization of MMA is coupled with the polymer molecular weight. Using an empirical correlation, the so-called Mark-Houwink equation,[34] the shear viscosity could be calculated with the polymer molecular weight. According to this kinetic model, the molecular weight should influence the viscosity curve. In Figures 4 and 5, only the molecular weight profile in the static TCR (ω = 0) is dependent on the zero shear viscosity curve. Therefore, the correlation was not applied to the TCR, and the

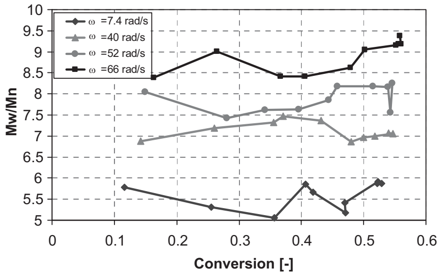

Figure 6.
Polydispersity index for the polymerization of MMA with 80 wt.% xylene.

polymerization in the TCR is not subject to these limits. More specifically, the molecular weight of the polymer is independent of the viscosity of the reaction medium.

The polydispersity index (M_w/M_n) is used to describe the width of the molecular weight distribution for a polymer disperse system. The widths of the molecular weight distribution for polymer samples from the batch polymerization with ($\omega > 0$) rotation of the inner cylinder are shown in Figure 6. For $\omega > 0$ (rotational inner cylinder), M_w/M_n is nearly constant during the polymerization. The distribution widths are placed differently to each other for the test with the rotational inner cylinder as it is a case of the molecular weight, and the polydispersity index depends on the rotational speed of the inner cylinder. The polymerization of MMA with 60 and 70 wt.% xylene was also the basis of experimentation in the TCR. The results were qualitatively similar to the 80 wt.% xylene. The solvent concentration was found to influence the width of the molecular weight of polymer samples as M_w/M_n decreases with the increase of the solvent concentration. Therefore, the distribution width for the polymerization with 80 wt.% is narrower than with 60 wt.% xylene.

Kinetic Modelling

The kinetic model of the batch polymerization of MMA has been presented in Eqs. 7, 8, 9, and 10. According to the kinetic model, the polymer conversion is calculated as a function of the reaction constant, monomer concentration and initiator concentration. The chain transfer was not observed in this study. It thus appears that reaction temperature and reactant properties influence the parameter $k = k_p/\sqrt{k_t}$. In addition, k basically depends on the process parameter, angular velocity of the inner cylinder and the solvent concentration for this work. In this model, the constant k is unknown. The parameter k could be determined by fitting in the experimental data. Here the decomposition rate constant $k_d = 8 \cdot 10^{-5}$ s^{-1} [35] and initiator efficiency $f = 0.5$ [25] were used for the modelling. The kinetic model with the resultant k and the polymer conversions with different rotational speeds of the inner cylinder and solvent concentrations are shown in Figure 7.

In Figure 7a and 7b, the model is not in very good agreement with the experimental data for very low polymer conversions (t < 120 min). It can be seen for t > 120 min min that the kinetic modelling and the experimental results are almost identical, because at the low rotational speed, the mass transfer of monomer towards radicals in TCR is very weak, and it is almost closed to the polymerization in the static TCR ($\omega = 0$). With 80 wt.% xylene, the model fitted the experimental data quite well. The values of the constant k for different rotational speeds and solvent concentrations were found and suited the experimental results.

In Figure 8, a comparison of the k values for the polymerization of MMA in the TCR with different solvent concentrations is shown. It can be seen that each constant k behaves in a parallel way with each different solvent concentration. It increases with the increase of the angular velocity of the inner cylinder. This behaviour has not been reported before and should be named "hydrodynamic activation". Furthermore, k decreases with the increase of the solvent concentration.

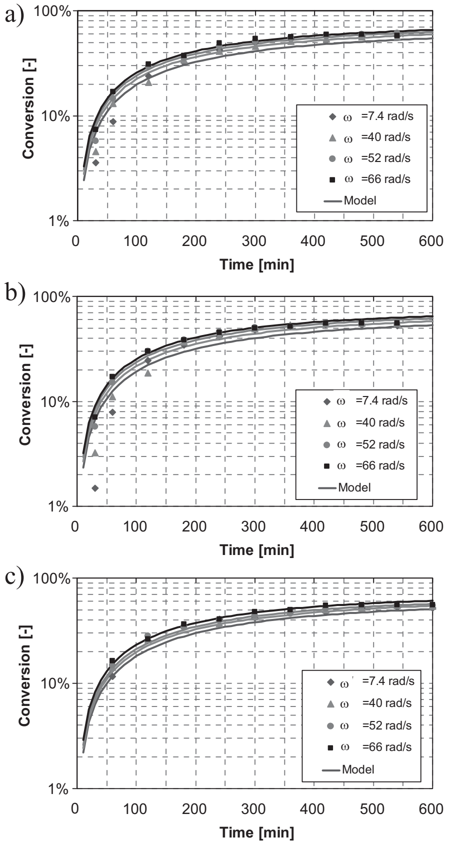

Figure 7.
Conversion versus reaction time for the MMA solution batch polymerization with different solvent concentrations: a) with 60 wt.% xylene; b) with 70 wt.% xylene; and c) with 80 wt.% xylene.

Conclusion

Hydrodynamic activation of batch solution polymerization of premixed MMA with xylene in the Taylor-Couette reactor at 80 °C has been investigated theoretically and experimentally. The experiments were performed in a TCR specially designed to induce the polymerization reaction in the gap between two concentric cylinders. The flow behaviour during the reaction exhibits transient states ranging from turbulent Taylor vortices (TTV) to laminar Couette flow (LCF), as the radial Reynolds number decreases with the increase of the viscosity of the reaction medium in the reactor. For a given solvent concentration, the Reynolds number was found to increase with the increase of the angular velocity of the inner cylinder. In the TCR, the presence of a rotational inner cylinder influences the molecular weight both qualitatively and quantitatively. Under static conditions ($\omega = 0$), the molecular weight increases significantly with increasing conversion, while there is poor heat and material transfer. Compared to the static TCR ($\omega = 0$), there is only weak dependence of the molecular weight as a function of the rotation of the inner cylinder, the molecular weight being almost constant. However, the zero shear viscosity is independent of the angular velocity of the inner

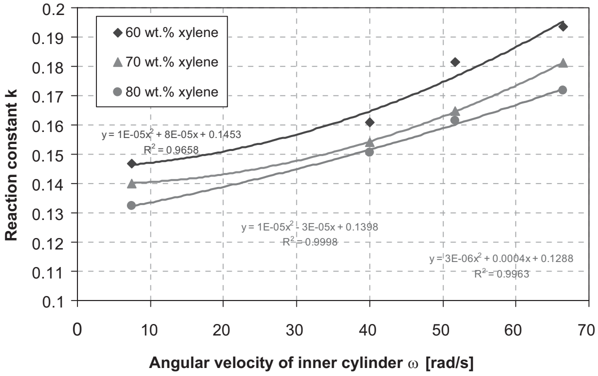

Figure 8.
Polymerization constant k as a function of the angular velocity of the inner cylinder and the solvent concentration.

cylinder. The polydispersity index (M_w/M_n) increases with the increase of the angular velocity of the inner cylinder. Using a kinetic model of the batch polymerization of MMA, the polymerization rate constant $k = k_p/\sqrt{k_t}$was determined by fitting in the experimental results. The model is in rather good agreement with experimental data. Therefore, the constant *k* increases with the increase of the rotational speed of the inner cylinder, and decreases with the increase of the solvent concentration.

The hydrodynamic activation is used to represent the polymer product properties, which would depict the influence of the process parameters on the batch polymerization of MMA in the Taylor-Couette reactor.

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Appendix A

A Simple calculation of the maximum temperature difference between the gap and the water film:

- Heat of polymerization of MMA is 55 kJ/mol [25]; half time of AIBN is 144 min at 80 °C.
- Reactor parameters: $d_i = 88.6$ mm, $d_o = 100$ mm, $L = 390$ mm
- Thermal conductivity: $\lambda_{stainlesssteel} = 42\frac{W}{m\cdot K}$, $\lambda_{mixtureinthegap} \approx 0.6\frac{W}{m\cdot K}$ $\dot{Q}_{Polymerization} = 8$ W

Energy dissipation: $P_{diss.} = \eta_{\max.} \pi^2 \frac{d_i^3 \cdot n_{\max.}^2}{\delta} \cdot L = 52\text{W}$ with $\eta_{\max} = 1Pas$ and $\omega_{\max} = 66\frac{rad}{s}$

$$\Delta T_{\max.} = \frac{P_{diss.} + \dot{Q}_{Poly.}}{A \cdot k}$$

Heat transfer surface area:$A = \pi \cdot (d_i + \delta) \cdot L = 0.115m^2$

Heat transfer coefficient: $k = \frac{1}{\frac{\delta/2}{\lambda_{mixture}} + \frac{\delta}{\lambda_{Steel}}} = \frac{1}{\frac{2.85\cdot 10^{-3}m}{0.6\frac{W}{mK}} + \frac{5.7\cdot 10^{-3}m}{42\frac{W}{mK}}} = 205\frac{W}{m^2K}$

$$\Delta \text{T}_{\max.} = 2.5\text{K}$$

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