Continuous Reactor Concepts with Superimposed Secondary Flow – Polymerization Process Intensification

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Summary: Different unconventional continuous polymerization reactor concepts with superimposed secondary flow are presented. Exemplary polymerization reactions and the residence time distributions are discussed. In the case of the Taylor reactor polymerization process intensification is demonstrated by examples of emulsion and micro-emulsion polymerization which actually results in an increase in space time yield of up to a factor of 50.

Keywords: fast emulsion polymerization; mixing; polymerization; residence time distribution

Introduction

One important task of polymerization process intensification is to invent and design new advantageous reactor concepts. Subsequently, such reactor concepts have to establish in continuous processes. They can help, when high heat flow rates are coupled with high viscosity increase, which is typical for polymerization processes. In this case it is expensive to realize a turbulent flow regime in order to ensure narrow residence time distributions. Therefore, agitators or static mixers are widely used.[1] When polymer wall fouling occurs or in the case of product changes the built-ins make it difficult to clean the reactor system. Under these circumstances reactor concepts with superimposed secondary flow can be the better choice.

Mankind has used superimposed secondary flow for many centuries. An early example is the use of trade winds. In our time superimposed secondary flow is generally employed in heat exchanging technology especially in coiled and ribbed tubes.[2] Recently corrugated tubes became more and more established.[3] The reason for this is an increased heat transfer coefficient because of an improved impulse transfer between main flow and wall flow in comparison to straight smooth tubes. From the polymer reaction engineering point of view an improved impulse transfer should result in a narrow residence time distribution of continuous reactors. This meets the requirements for achieving high conversion and high space time yield. Furthermore, in many cases polymer reaction engineers need high cooling capacities and subsequently high heat transfer coefficients. Thus heat exchangers with superimposed secondary flow can be interesting continuous chemical reactor concepts.

But superimposed secondary flow is not only used in heat exchanging technology. An example with improved mass transfer by superimposed secondary flow is the Taylor reactor concept.[4] While emulsion polymerization is speeding up mass transport becomes more and more important. That is why the Taylor reactor concept is investigated in the context of fast emulsion and micro-emulsion polymerization. As an example for suspension polymerization the torus reactor concept is presented.

Corrugated Tube Reactor Concept

Nowadays corrugated tubes are well established in heat exchanging technology. The

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Nusselt number Nu can be increased by more than 250 % in comparison to straight smooth tubes.[3] The reason for the increase in Nusselt number is the superimposed secondary flow because of the corrugated tube surface. In order to compare the corrugated and the straight smooth tube the conductivity was measured in inlet and outlet by using pulse signals.[5] The tube dimensions are given in Table 1.

The transfer function was calculated by folding the inlet and the outlet signals. Afterwards the resulting Bodenstein number Bo was determined by the least square method using the dispersion model with the density function E and the reduced time Θ.

$$E(\Theta) = \frac{1}{2 \cdot \Theta} \cdot \sqrt{\frac{Bo}{\pi \cdot \Theta}} \cdot e^{-\frac{(1-\Theta)^2 \cdot Bo}{4 \cdot \Theta}}$$

The Bodenstein number used in this context is defined as,

$$Bo = \frac{u \cdot L}{D_{ax}} = \frac{L^2}{\tau \cdot D_{ax}}$$

where u is the flow velocity, L and D_{ax} are the tube length and the axial dispersion coefficient, respectively. The mean residence time τ is adjusted according to the reaction time and the intended monomer conversion.

The characteristic dimensionless number in order to describe the flow regime is the Reynolds number Re which is the product of fluid velocity u and the tube diameter d divided by the kinematic viscosity ν

$$Re = \frac{u \cdot d}{\nu} = \frac{L \cdot d}{\tau \cdot \nu}$$

In straight smooth tubes laminar and near laminar flow regimes and the corresponding residence time distributions are well investigated.[6] Thus the residence time distribution of the corrugated tube was determined and the corresponding Bodenstein numbers were evaluated (Fig. 1).

Close to a Reynolds number of 1600 a strong increase in Bodenstein number is observed. However, chemical engineers are interested in high Bodenstein numbers particularly at Reynolds numbers lower than 100, in order to obtain high monomer conversion at reasonable tube length. Therefore, the setup was changed to pulsed corrugated and pulsed straight tubes.

Table 1.
Dimensions of the investigated corrugated tube.

	Corrugated tube	Straight smooth tube
Length	2950 mm	2950 mm
Diameter	23.8 mm*	23.7 mm
Helix angle	21.26°	
Helix distance	5.0 mm	
Helix depth	1.6 mm	

* Characteristic diameter.

Reactor Concepts of Pulsed Straight Smooth and Corrugated Tubes

It is well known that pulsing in straight smooth tubes can avoid wall fouling and narrows the residence time distribution.[7] Quite as well, pulsing increases the Bodenstein number significantly in corrugated tubes. Especially in the range of Renolds numbers lower than 1600 the advantage is considerable in comparison to the experiments without pulsing.

Consequently, it is necessary to compare a pulsed straight smooth tube with a pulsed corrugated tube. When pulsing a reactor, the frequency and the amplitude have to be considered as two additional parameters. A pulsating device was built up and measurements for the tubes of Table 1 were carried out (Fig. 2).

The results for the investigated ranges show the advantage of a pulsed corrugated tube in comparison to the straight smooth tube (Fig. 3). This is especially remarkable, since no special adopted corrugated tube was in use. Therefore, a large optimization potential for the application of corrugated tubes in chemical reaction engineering is expected.

Straight and Bent Helical Coiled Tubes

In heat exchanging technology coiled tubes are well known. They are also used in micro mixing technology.[8,9] In comparison to straight smooth tubes, coiled tubes are a further example of improved impulse transfer from near wall flow to main flow. If a liquid flows through a coiled tube, Dean

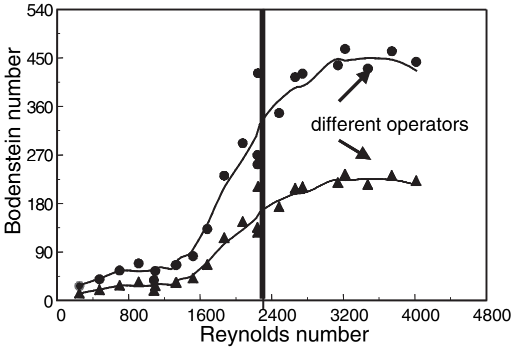

Figure 1.
Bodenstein number versus Reynolds number; measurements of two operators.

vortices will come up (Fig. 4). These are counter-rotating vortices, which generate mixing in perpendicular direction to the main flow. Such a reactor uses superimposed secondary flow pattern for enhancing mass and heat transport over the cross-section of the tubular reactor. It has the advantage of no parts in motion, no dead water zones and no gas phase. Comparatively moderate and evenly distributed shear rates and the large heat exchange area are of special interest for emulsion polymerization processes.

If helical coiled tubes are bent, the curvature of the tube will not change, but the orientation of the Dean vortices. Passing a tube bend, fast flowing fluid compartments change into slow and vice versa. This should further result in a narrow residence time distribution. Thus, the aim was to build up a reactor that consists only of knees. This led to the so-called bent reactor or wicker tube reactor. (Fig. 4 on the right).

Tracer experiments were carried out to compare the coiled tube reactor with the bent reactor.[10] For the bent reactor significantly higher Bodenstein numbers were determined (Fig. 5).

Especially the very high Bodenstein numbers at Reynolds numbers lower than 100 make this continuous reactor concept more attractive for polymerization technology in comparison to helical coiled tube reactors.[11–13]

Torus Reactor Concept

Literature reveals a lot of activities to polymerize suspensions in a continuous operation mode. A search for continuous suspension polymerization gives at least

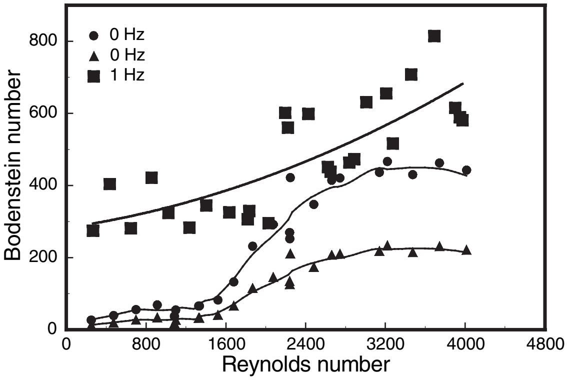

Figure 2.
Comparison of Bodenstein numbers of pulsed and non-pulsed corrugated tube (dimensions see Table 1).

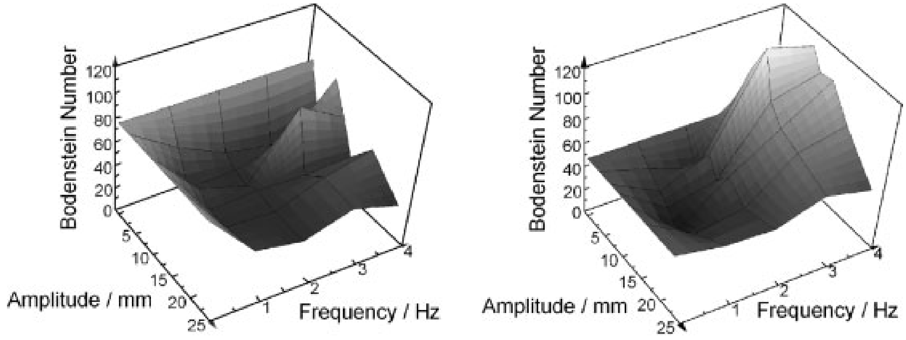

Figure 3.
Comparison of Bodenstein number from pulsing experiments in the straight smooth tube (on the left) and corrugated tube (on the right).

499 hits in scifinder scholar. Nevertheless, continuous suspension polymerization processes are not well established in the polymer reaction engineering community. Therefore, we looked for a reactor with superimposed secondary flow for suspension polymerization.

Tanaka proposed the torus reactor as a suitable device for batch-wise suspension polymerization.[14] For stirred suspensions the particle size distribution is determined by droplet break-up and coalescence processes. In a torus reactor the stirrer has to move the dispersion through the reactor and to superimpose a secondary flow. The high symmetry of the torus reactor and the forced circulation in it should thereby result in a uniform particle size distribution because of the uniform particle history. So a torus reactor was built up for suspension polymerization[15] (Fig. 6). First batch-wise suspension polymerization experiments were made at different stirrer speeds besides the detailed hydrodynamic characterization. (Table 2 and Fig. 7).

The torus reactor shows almost plug flow characteristics with Bodenstein numbers around 150. Polystyrene beads were polymerized at a volume fraction of the monomer phase of 10 to 20 % with good reproducibility of the particle size distribution. But the particle size distribution itself is too broad in comparison to products obtained in stirred tank reactors.

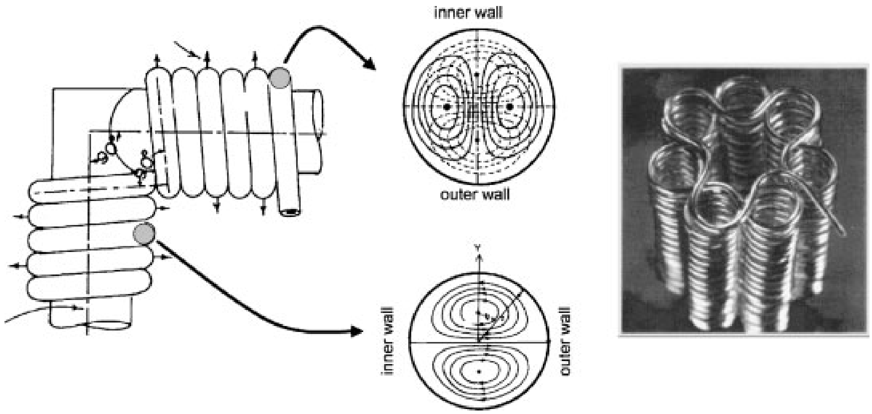

Figure 4.
Dean vortices in coiled tubes and the bent reactor on the right.

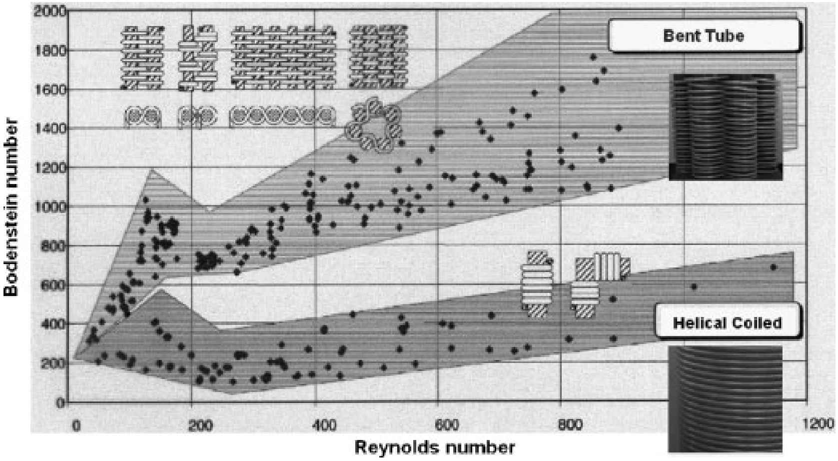

Figure 5.
Back mixing in helical coiled and bent tube reactors.

The explanation is given by the nature of the superimposed secondary flow: the rotating stirrer induces gravity forces and thus a density gradient. Therefore, the localization of the dispersed phase is inhomogeneous. The highest content of the dispersed phase is near the torus main radius and the particle history is uneven. Indeed, baffles make the particle size distribution narrower. The disturbed secondary flow seems to be the reason. Thus, a torus reactor with superimposed secondary flow is not the best choice for suspension polymerization although it has some advantages with regard to the specific cooling area.

The Taylor Reactor Concept for Fast Emulsion Polymerization

''Fast'' emulsion polymerization means to polymerize in emulsion in less than 15 minutes to complete conversion and is an interesting field to investigate. Up to now mass transport limitations are avoided by a slow reaction rate. Little experience exists on reliable mass transfer coefficients of different monomers. Furthermore, the monomer solubility in polymer differs for different monomers. That is why semibatch operation under starved conditions is the actual method to produce lattices of different co-monomer compositions. In order

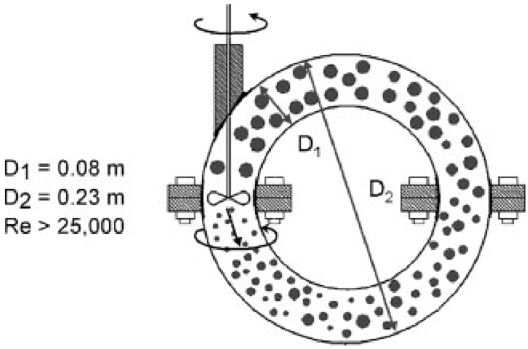

Figure 6.
Schematic sketch of the torus reactor for suspension polymerization.

Table 2.
Recipe for suspension polymerization T = 353K, reaction time 6 h.

	Mass
Stabilizer PVA 100000	0.460 g/0.800 g
Styrene	430.0 g/750.0 g
BPO	1.1 wt.-%
Water	3588.0 g/3207.0 g

to run an emulsion polymerization faster we started with emulsion and micro emulsion homo-polymerization.

Besides the reaction system an appropriate flexible reactor was necessary. Couette and Mallock observed hydrodynamic instabilities in the liquid filled gap between two concentric cylinders if the inner cylinder rotates. Sir G. Taylor made the first mathematical description in 1923. In consequence, the counter rotating vortices are called Taylor vortices.[16]

A Couette-Taylor reactor consists of a rotating inner cylinder and a fixed outer cylinder with an inlet at the bottom and an outlet at the top. The chemical reaction is carried out in the gap volume Fig. 8

The characteristic number for a Taylor reactor is the Taylor number *Ta* with the gap width d, the rotational speed ω, the inner cylinder radius r_i and the kinematical viscosity ν

$$Ta = \frac{\omega_i \cdot r_i \cdot d}{\nu} \sqrt{\frac{d}{r_i}}$$

At very low rotational speed of the inner cylinder the laminar flow in con-

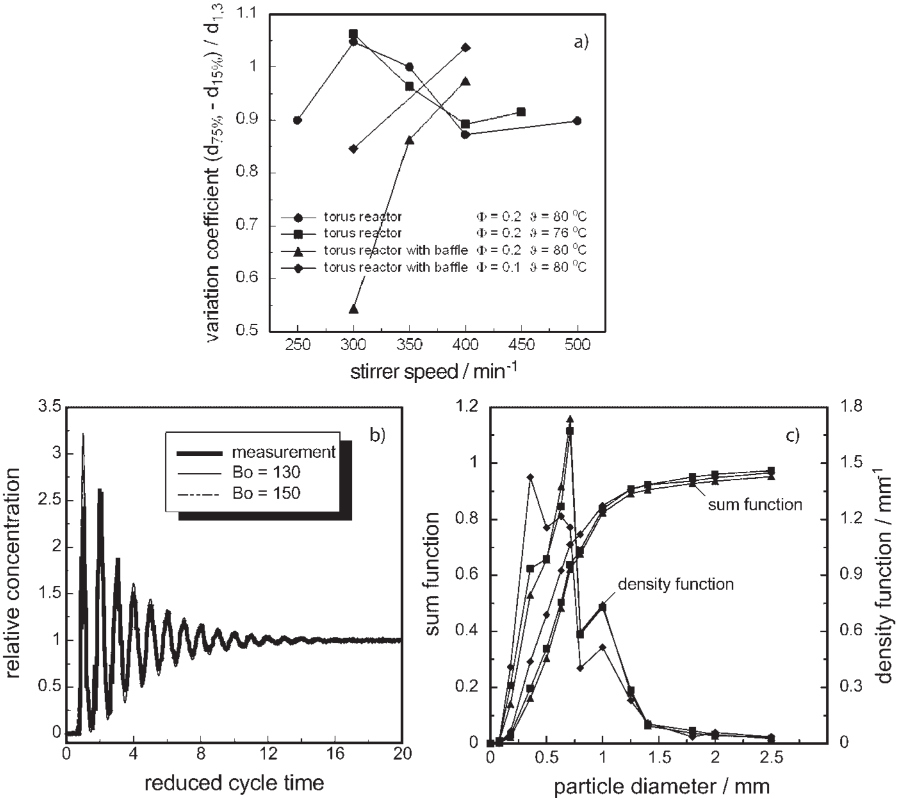

Figure 7.
a) Particle size variation coefficient in the torus reactor, b) Mixing characteristics, c) Reproducibility of the particle size distribution.

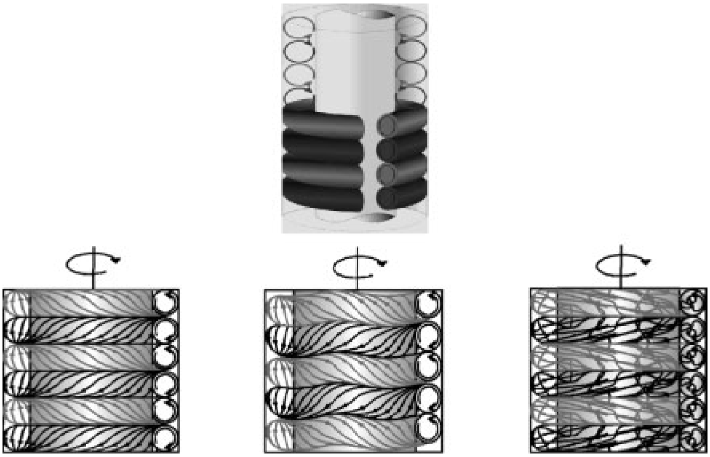

Figure 8.
Sketch of a Taylor reactor with laminar, wavy and turbulent flow patterns.

centric layers, the so-called Couette flow, is coming out. With increasing rotational speed the Ta number increases, too. When the Taylor number exceeds the critical value of 42 the laminar Taylor vortex flow will come up. Finally the wavy Taylor vortex flow is formed when the quotient of both cylindrical diameters exceeds 1.4. At high rotational speed the turbulent Taylor vortex flow exists. If a liquid flows through a Taylor reactor the hydrodynamics will correspond with the different Taylor vortex flow patterns and change from tubular reactor behavior over tanks in series to continuous stirred tank reactor characteristics. The Taylor reactor is therefore a very flexible device with tunable resistance time distribution.[5,10,16–19] In order to run emulsion polymerization faster a continuous laboratory plant with a horizontal Taylor reactor was built up.[5] Table 3

Heat removal is one of the limiting factors in polymer reaction engineering. For a fast emulsion polymerization an appropriate heat transfer coefficient is necessary. Therefore, the heat transfer coefficient was determined for the Taylor reactor. The characteristic dimensionless number for the heat transfer is the Nusselt number Nu. The Nusselt number is equal to the product of the product side heat transfer coefficient α and a characteristic length l divided by the heat conductivity λ

$$Nu = \frac{\alpha \cdot l}{\lambda}$$

In the case of a Taylor reactor the characteristic length is equal to the hydraulic diameter d_h, which is equal to twice the difference between the outer and the inner radius, r_a and r_i

$$d_h = 2 \cdot (r_a - r_i)$$

A product side heat transfer coefficient of $\alpha = 590$ W/(m$^2 \cdot$K) is obtained with $Nu = 9.7$, $d_h = 0.0104$ m and $\lambda = 0.633$ W/(m $\cdot$ K). Together with a wall thickness of 2 mm this leads to an overall heat transfer coefficient of 283 W/(m$^2 \cdot$K). The heat transfer area is 8 to 16 times larger than for a comparable stirred tank reactor of the same volume. Even if a product side heat

Table 3.
Dimension of the continuous laboratory Taylor reactor with four cooling zones.

	Continuous Taylor Reactor
Volume	700 ml
Pressure limit	9 bar
Length	1.1 m
Gap width	5.2 mm
ϕ-inner cylinder	32 mm

Table 4.
Recipe for n-BMA continuous emulsion polymerization.

	Weight fraction in %
n-BMA	10
Water	89.64
SDS	0.16
$NaHCO_3$	0.1
PPS	0.1

transfer coefficient of optimistic 4000 $W/(m^2 \cdot K)$ is assumed for the stirred tank reactor, only one third of the necessary temperature difference for equivalent cooling capacity results for the Taylor reactor. Thus, the Taylor reactor should be a suitable device for fast running continuous emulsion polymerization with regard to heat removal and residence time distribution.

N-butyl methacrylate (n-BMA) is polymerized in first experiments of a continuous emulsion polymerization at 80 °C and different mean residence times from 7 to 12 minutes (Tab. 4). In this experiments the polymerization was run with *in situ* latex particle formation within the continuous Taylor reactor. Mean particle sizes of about 60 nm were obtained.

Almost complete conversion was achieved in the range from 9 to 12 minutes for the mean residence time. The vertical lines in Figure 9 indicate the moments of changing the feed rates. Stationary monomer conversion is reached rapidly which corresponds to a narrow residence time distribution. During the whole operation time nearly no wall fouling was observable.

n-BMA is a fast reacting monomer. At 70 °C the chain propagation rate constant is $k_P = 970$ l/(mol · s). For the slower reacting monomer styrene comparable reaction speed can be achieved in emulsion polymerization by increasing the reaction temperature and/or the specific number of latex particles. Therefore, we switched to micro emulsion polymerization of styrene. In order to avoid any problems with polymer wall fouling rather low monomer content is used in this recipe (Tab. 5).

A micro emulsion is a thermodynamic stable emulsion and because of a higher amount of stabilizer there are reduced problems with wall fouling. Due to the usage of a water soluble initiator the micro emulsion system of Table 5 is regarded as a good model system, to check the opportunities of fast emulsion polymerization.

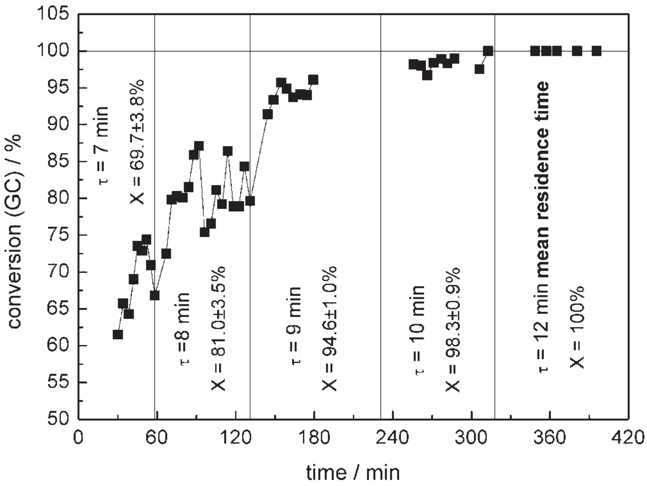

Figure 9.
Conversion of n-BMA emulsion polymerization in a continuous Taylor reactor at different mean residence times.

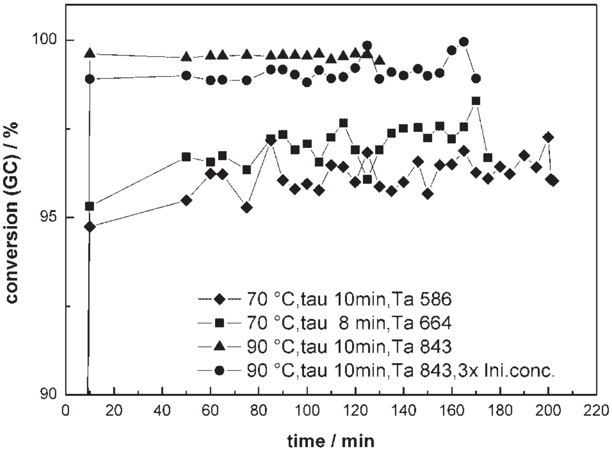

Figure 10.
Conversion of styrene micro emulsion polymerization in a continuous Taylor reactor at different reaction conditions and mean residence times of 8 and 10 min.

Styrene has a chain propagation rate constant of $k_P = 460$ l/(mol · s) at 70 °C. At this temperature the stationary monomer conversion reaches a level of about 96% +/− 1% at mean residence times of 8 or 10 min (Fig. 10). The average latex particle diameter is 29 nm. In order to reach almost complete conversion reaction temperature is increased to 90 °C.

Increasing the reaction temperature up to 110 °C make it possible to reduce the mean residence time to only 5 min and keep the monomer conversion almost complete (Fig. 11).

Now we are able to operate emulsion and micro emulsion polymerization very fast. Fast emulsion polymerization make it possible to use tall tubes for higher Reynolds numbers with an acceptable length. Thus we are preparing the comparison of classical tube reactors with the presented new reactor concepts.

Table 5.
Recipe for continuous micro emulsion polymerization of styrene.

	Weight fraction in %
Styrene	6
Water	92.3
SDS	1.5
n-pentanol	0.2
PPS	0.014

Conclusions

In many cases polymerization processes benefit from superimposed secondary flow. Even in simple tubular reactors superimposed secondary flow can mix in perpendicular direction to the main flow at moderate shear fields. Thus the residence time distribution becomes narrower without any built-in. Furthermore, dead water zones are avoidable and all this with a large product side heat transfer coefficient.

At low Reynolds numbers bending is of advantage in comparison to coiling. When using corrugated tubes at low Reynolds numbers pulsing is necessary. In comparison to pulsed straight tubes pulsed corrugated tubes perform better. A significant narrowing in residence time distribution is possible.

Of the presented reactor concepts the Taylor reactor concept is the most flexible due to variable stirrer speed. Residence time profiles from almost plug flow tubular like to tanks in series to continuous stirred tank like characteristics can be realized. Fast emulsion and micro emulsion poly-

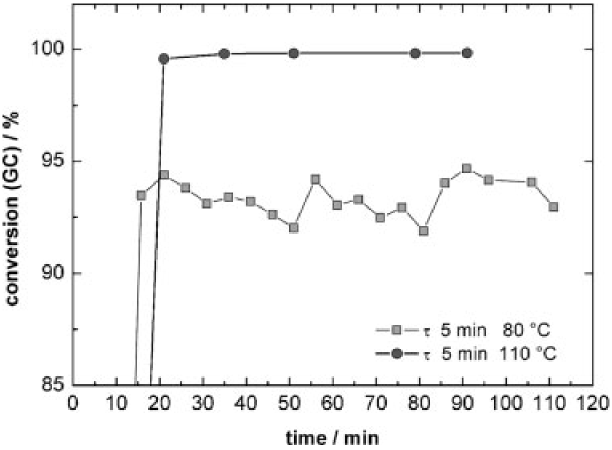

Figure 11.
Conversion of styrene micro emulsion polymerization in a continuous Taylor reactor at different reaction temperature and a mean residence time of 5 min.

merization profit from superimposed secondary flow. Space time yield is enhanced by a factor of 48 in comparison to conventional semibatch emulsion polymerization. This is regarded as a significant contribution to polymerization process intensification.

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