

# Investigation of Shear Effects on Styrene Free Radical Polymerization Using a Narrow Channel Reactor

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**ABSTRACT:** Spinning disc reactor technology has been demonstrated to achieve significant enhancements in the rates of free radical polymerization. It is believed that these enhancements are related to the centrifugal and shear conditions that exist on the disk and it is the objective of this study to elucidate the role of shear in thin films in a plug flow regime. Polymerizing systems have been subjected to shear fields in the range of 0.4 to 2,173 s<sup>-1</sup> and comparisons between conversion profiles and polymer product properties have been made. It has been found that shear fields have little or no effect on these systems while the reaction is in the

kinetically controlled regime and it is concluded that the observed rate enhancements of free radical polymerization on a spinning disk are not largely attributable to the high rates of shear experienced by the thin film as it traverses the disk. Our studies therefore continue to assess the role of flow divergence and centrifugal extension in the kinetics of polymerization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1365–1369, 2004

**Key words:** mixing, polystyrene, radical polymerization, shear

## INTRODUCTION

In this work the influence of shear on thin films flowing in a plug flow regime has been investigated. The work has been completed as part of an ongoing investigation aiming to elucidate the polymerization mechanism occurring on a spinning disc reactor (SDR). Spinning disc reactor technology has been demonstrated to achieve significant enhancements in free radical polymerization rates.<sup>1</sup> This technology exploits the benefits of centrifugal force, which produces thin highly sheared films due to radial acceleration. It is believed that the excellent mixing as well as plug flow characteristics should aid in producing polymer products characterized by narrow molecular weight distribution.

The hydrodynamic regime on a SDR is very complicated. The highly sheared thin film acts to promote heat and mass transfer. The shear rates are sufficiently high to disentangle the polymeric products and promote parallel flow of the chains. The centrifugal field created by the rotation may act to extend the free draining polymer chains to a more linear structure. The geometry of the disk creates divergent streamlines that may play a role in controlling the termination mechanism. Backmixing is minimized on the SDR such that the fluid flows in a plug flow regime. Thus to gain understanding of the system it is important to try

to isolate each of the factors to assess which is responsible for the dramatic increase in reaction rate measured for free radical polymerizations conducted on a SDR.

Imposing shear fields on polymerization systems can lead to polymer alignment and a reduction in the viscosity of the system (i.e., shear thinning). For condensation polymerization this alignment has been shown to increase the overall reaction rate and to produce a higher molecular weight product for systems in which the product formed has a rigid rod-like backbone.<sup>2</sup> Here it is thought that the shear field acts to align the rod-like reactants causing near parallel flow thus increasing the probability of two end groups coming together and reacting. Birefringence experiments conducted on these systems observed increasing alignment and reaction rate with shear rates up to 400 s<sup>-1</sup>.

The influence of shear fields on free radical batch polymerization systems has also been investigated using rheokinetic studies. This work revealed that shear has no effect on the system in the early stages of the polymerization when the system is thought to be kinetically limited. However, it has been found that, if the polymerization is conducted under sufficient shear, then the onset of the gel effect can be reduced if not completely eliminated,<sup>3,4</sup> resulting in a final product with a narrower molecular weight distribution.

In this work a microchannel reactor has been used to quantify the effect of shear on a polymerizing thin film in a plug flow regime. The dimension of the inner diameter of the capillary tube used has been chosen as twice a typical film thickness on a SDR. This was

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chosen so as to produce a similar velocity profile and thus similar shear distribution as would be expected in the thin film. This analogy assumes that the unattached top surface of the film on the SDR does not greatly affect the velocity profile.

Boodhoo et al.<sup>5,6</sup> have conducted extensive studies into the rates of polymerization of styrene in both batch reactors and SDRs. The work quantified rate enhancements observed when using a SDR and showed how the polydispersity of the SDR product remained constant, even beyond conversions at which the gel effect would be expected to result in broadening of the weight distribution of the products.

Experiments were conducted with a feed mixture comprised of 7.18 mol/L styrene, 1.57 mol/L toluene, and 0.052 mol/L benzoyl peroxide (BPO). In each experiment the reaction took place in a batch reactor to a predetermined extent and was then fed onto a SDR. The final product was quenched and then analyzed. Using this technique both the time conversion behavior of the batch system and SDR were measured. In the present microchannel work the feedstock was of identical composition, thus allowing comparisons of the results gained from this work to batch and SDR systems.

### POLYMERIZATION MECHANISM

The mechanisms for chemically initiated free radical polymerization are well documented,<sup>7</sup> thus only the briefest outline is given here. The overall polymerization process consists of three well-defined steps: initiation, propagation, and termination. Initiation is brought about by the attack of monomer by free radicals that have been generated by the cleavage of an initiator, as shown in eqs. (1) and (2):



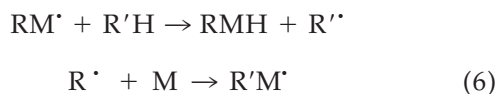
Propagation proceeds by the successive addition of monomer as shown in eq. (3):



For each addition of monomer to the growing chain there is also a probability that the chain may undergo a reaction that prevents further monomer addition to the chain. This may occur by a bimolecular process in which two active chains react with each other to form an inactive polymer. Two distinctive reactions may be defined: combination or disproportionation, which are shown in eqs. (4) and (5):



Termination of active chains may also be brought about by transfer reactions to monomer, solvent, polymer, or initiator. Such reactions result in the early termination of propagating chains with the result that polymer molecular weights are reduced. In a well-designed polymerization, selection of components will minimize these reactions, although one may deliberately add an active chain transfer agent to control molecular weight. Such compounds should ideally give rise to free radicals that have similar reactivity to the growing polymer chain, thus polymerization rate is virtually unaffected and the only result is a lowering of molecular weight. Equation (6) depicts this reaction:

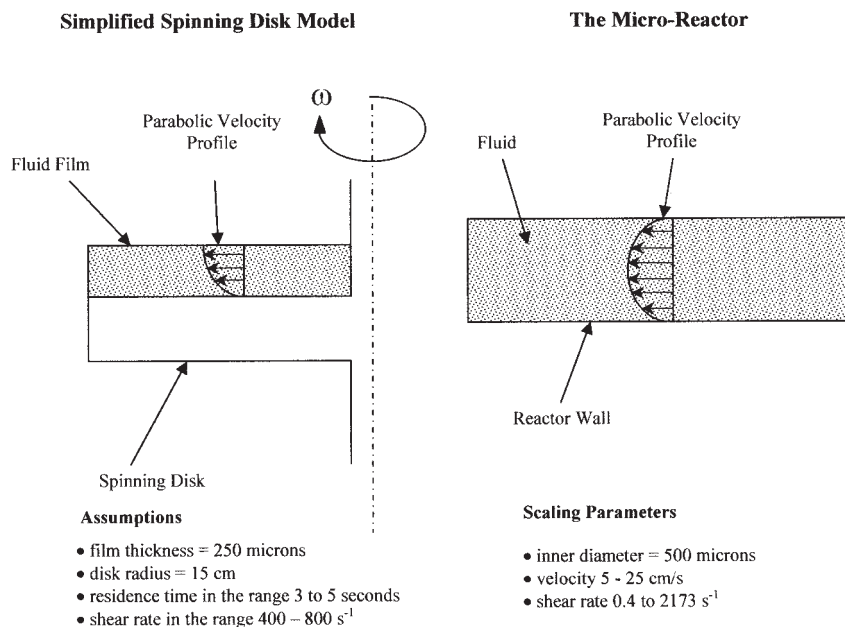


### EXPERIMENTAL APPARATUS

The apparatus used to assess the influence of shear on the rate of polymerization of a BPO-initiated styrene polymerization is illustrated in Figure 1. The feed mix was prepared by mixing 200 mL of styrene monomer with 40 mL of toluene to which 3 g of BPO was added. This produced a feed of molar composition: 7.28 mol/L styrene, 1.57 mol/L toluene, and 0.052 mol/L BPO. Once the feed was prepared it was added to a 500-mL conical flask, which acted as the feed vessel. The inlet pipe from the HPLC pump was placed in the vessel and the top was sealed.

During the experimental tests the monomer feed mix was drawn from the feed vessel using an Alltech 426 HPLC pump. The mixture was then pumped through the microchannel reactor with a known flow rate. The reactor was situated in a well-stirred thermostatically controlled water bath. Heat transfer calculations based on this system predict negligible temperature differences between the reacting monomer and the water bath, thus allowing the reactor to operate under near isothermal conditions. After exiting the reactor the fluid contacted the probe of the ATR FTIR probe where conversion was quantified. Samples were also collected at this point for molecular weight and polydispersity analysis using gel permeation chromatography (see Fig. 2).

The microreactor was constructed by connecting 5-m lengths of 0.5 mm i.d., 1.59 mm o.d. stainless steel capillary tubing with Swagelok zero dead volume couplings. Various numbers of identical sections were joined until a reactor of the desired length was attained. As the mixture flows through the reactor and the reaction proceeds, the viscosity increases. The pumping pressure generated from the HPLC pump was found to be sufficiently high to maintain a constant flow rate even for the longest reactor lengths and highest conversions achieved in these tests.



**Figure 1** A comparison between the velocity profile on the SDR and microchannel reactor.

The conversions achieved were measured using a Mettler Toledo IR-4000 attenuated total reflection (ATR) spectrometer. This infrared device utilizes a conduit to separate the probe from the detector. This allowed the probe to be placed directly in the outlet stream, facilitating continuous measurements of both conversion and transient behavior between experimental conditions. To gain accurate composition data the spectrometer was calibrated to translate peak heights to actual component concentrations. The calibration samples were prepared by dissolving known amounts of polystyrene (melt index 12) in styrene with vigorous stirring. The QuantIR software supplied with the spectrometer was used to equate peak heights to the mass fraction of each component in the calibration samples. The QuantIR software compares the spectra collected from the calibration mixes to select optimum representational peaks for each component and then to fit functions of peak height to actual concentration. Six calibration samples were prepared with polystyrene fractions up to 60% to minimize any errors due to nonlinearities in peak height to sample mass fractions ratio.

Molecular weights and molecular weight distributions were measured using a Polymer Lab gel perme-

ation chromatograph equipped with a RI detector. The chromatograph was calibrated using standard calibration polymers to equate retention time to polymer molecular weight. The samples collected from the reactor exit were dissolved in THF to produce solutions with sample-to-THF ratios of 1 : 200 (g/g). An auto-injector was used to introduce the solutions onto the GPC column.

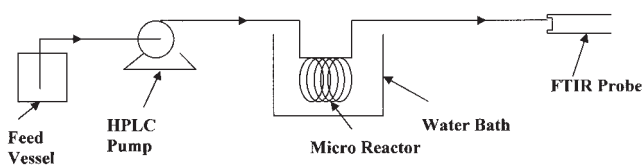
## RESULTS AND DISCUSSION

To assess the influence of shear on the kinetics of polymerization a series of experiments have been conducted to directly compare time conversion behavior and the polymer produced under different shear fields. To calculate a characteristic shear rate for each system the wall shear rate has been used. This is simply calculated using eq. (7).

$$\gamma = \frac{8V}{d} \quad (7)$$

Where  $\gamma$  is the shear rate (s<sup>-1</sup>),  $V$  is the bulk velocity (m/s), and  $d$  is the tube diameter (m). In the first set of experiments the reactor length and velocity were adjusted such that the residence time in the reactor was constant. The experimental conditions, conversions achieved, and average molecular weight of product ( $M_n$ ) and polydispersity index (PDI) are given in Tables I and II.

In both cases it can be seen that shear has a negligible effect on both time conversion behavior and polymer product. This result illustrates how at low conversion the reaction is kinetically limited, thus im-



**Figure 2** Schematic of the experiential arrangement.

TABLE I  
Conversions Achieved with a Constant Residence Time of 4.91 min with a Shear Rate of 271 to 2,172 s<sup>-1</sup>

Flow rate (cm <sup>3</sup> /s)	i.d. (mm)	Length (m)	Shear rate (s <sup>-1</sup> )	Conversion (%)	M <sub>n</sub> (g/mol)	PDI
0.2	0.5	5	271.6	4.32	24,136	1.62
0.4	0.5	10	543.2	4.42	24,526	1.64
0.8	0.5	20	1,086.5	4.28	24,458	1.60
1.6	0.5	40	2,173.0	4.26	24,237	1.64

posing smaller and smaller mixing timescales has no effect. The results also seem to imply that the shear rate does not affect the rate of initiator dissociation or improve the initiator efficiency,  $f$ . If either of these factors were related then one would expect to see a variation in the average molecular weight and time conversion behavior.

Experiments were also conducted using a 4.2 mm i.d. tubular reactor. In this case the length was 0.56 m such that the internal volume was slightly less than the 40-m-long microreactor. In this case a 2-m-long section of capillary tubing was used upstream of the tubular reactor to act as a preheat section; this capillary section increased the internal volume of the tubular reactor system to match that of the 40-m-long microreactor. The experimental conditions and results achieved for the 40-m-long capillary reactor and tubular reactor are given in Tables III and IV.

It can be seen that once again shear has little influence on the time conversion behavior or polymer product. For the case of the tubular reactor the conversion is slightly higher in all cases. It is thought that this may be attributable to lower rates of heat transfer between the process fluid and reactor wall. In this case the process fluid may be slightly hotter than the waterbath and hence acts to increase the rates of initiator decomposition and polymerization.

### Comparison to batch reactor data

Boodhoo et al.<sup>5,6</sup> has conducted extensive studies in rates of polymerization of styrene in both batch reactors and SDRs. The work quantified rate enhancements possible by using a SDR and showed how the polydispersity of the SDR product remained constant, even beyond conversions at which the gel effect would be expected to result in broadening of the weight distribution of the products. The conversions achieved in

the batch reactor are compared to the micro reactor and tubular reactor in Figure 3.

Superimposed on Figure 3 is the time conversion profile predicted from eq. (8) utilizing the rate constants calculated using eqs. (9)–(11), which have been taken from the literature.<sup>8–10</sup>

$$x = 1 - \exp \left\{ -2k_p \sqrt{\frac{f[I]_0}{k_d k_t}} \left( 1 - \exp \left\langle \frac{-k_d t}{2} \right\rangle \right) \right\} \quad (8)$$

where  $t$  is time (s),  $k_p$  is the rate of polymerization (mol/L s),  $k_d$  is the rate of initiator dissociation (s<sup>-1</sup>),  $k_t$  is the rate of termination (mol/L s),  $[I]$  is the initiator concentration at  $t = 0$  (mol/L), and  $f$  is the initiator effectiveness factor.

Published kinetic parameters applicable to free radical polymerization of styrene with BPO as initiator are

$$fk_d = 6.378 \times 10^{13} \exp \left( \frac{-29,700}{RT} \right) \quad (9)$$

$$k_p = 10^{7.630} \exp \left( \frac{-7,740}{RT} \right) \quad (10)$$

$$k_t = 1.255 \times 10^9 \exp \left( \frac{-1,675}{RT} \right) \quad (11)$$

As can be seen from Figure 3, in all cases the results from both the batch and flow experiments compare amazingly well. The closeness between the experimental results and those predicted using eq. (8) illustrates how this system is kinetically controlled over the conditions tested and that shear does not affect any of the phenomena occurring.

TABLE II  
Conversions Achieved with a Constant Residence Time of 9.8 min with a Shear Rate of 271 to 1,086 s<sup>-1</sup>

Flow rate (cm <sup>3</sup> /s)	i.d. (mm)	Length (m)	Shear rate (s <sup>-1</sup> )	Conversion (%)	M <sub>n</sub> (g/mol)	PDI
0.2	0.5	10	271.6	8.62	24,256	1.65
0.4	0.5	20	543.2	8.52	24,761	1.64
0.8	0.5	40	1,086.5	8.47	24,789	1.67

TABLE III  
Microreactor Results

Flow rate (cm <sup>3</sup> /s)	i.d. (mm)	Length (m)	Shear rate (s <sup>-1</sup> )	Residence time (min)	Conversion (%)
0.1	0.5	40	135.8	78.5	49.2
0.2	0.5	40	271.6	39.3	28.7
0.4	0.5	40	543.2	19.6	15.8
0.8	0.5	40	1,086.5	9.8	8.5
1.6	0.5	40	2,173.0	4.9	4.3

In this study the influence of shear on polymerization rates has been addressed. From the time conversion behavior it can be seen that the shear rate has little influence on reaction rate compared to the well-stirred batch reactor. This result implies that the system is not sensitive to rates of mixing, confirming previous findings that the reaction is kinetically limited until the latter stages. The second implication is that shear fields are not sufficiently strong to influence the termination mechanism. It is well known that shear fields can act to align polymer chains, which results in the phenomena known as shear thinning. However, in this case the alignment achieved seems to not affect the probability of two propagating polymer chains from terminating through bimolecular reactions. If the termination was either promoted or restricted one would expect a change in the average molecular weight of the product compared to the batch reactor. It is interesting to note that in both the batch and the microreactor work the polydispersity of the product is in the range 1.6 to 1.8, which is close to the statistical limit for termination through combination. Another interesting finding is that the shear rate does not affect the initiator efficiency,  $f$ . It is surprising that enhanced mixing does not enhance the probability of two cleaved benzoyloxy radicals from reacting with the monomer rather than reacting together to recombine or decarboxylate.

As mentioned earlier in this paper this work is part of an ongoing investigation aiming to elucidate the polymerization mechanism occurring on a SDR. The results gained in this study illustrate that there is no influence of shear rate on polymerization kinetics or product spectrum. This result is very useful as it allows further work to concentrate on the effect of a centrifugal field and flow

TABLE IV  
Tubular Reactor Results

Flow rate (cm <sup>3</sup> /s)	i.d. (mm)	Length (m)	Shear rate (s <sup>-1</sup> )	Residence time (min)	Conversion (%)
0.1	4.2	0.56	0.23	78.9	51.2
0.2	4.2	0.56	0.44	39.5	29.5
0.4	4.2	0.56	0.92	19.7	16.4
0.8	4.2	0.56	1.83	9.9	8.6
1.6	4.2	0.56	3.67	4.9	4.4

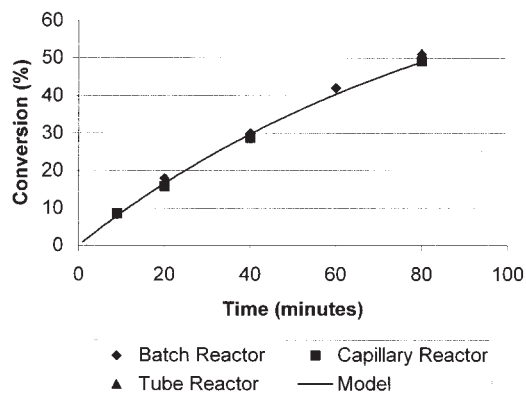


Figure 3 Time conversion profiles for the batch, capillary, and tube reactor.

divergence on polymerizing systems. It has been proposed that the centrifugal field and/or divergent flow characteristics may align two propagating polymer chains in such a way that termination through bimolecular reactions is severely hampered.<sup>1</sup> This postulation has been numerically simulated by assuming  $k_t = 0$ , that is that bimolecular termination reactions do not occur on the disk.<sup>11</sup> The findings of this simulation work illustrated how typical SDR conversion behavior could be explained by limited termination kinetics. The work predicted a rapid increase in radical concentrations as a function of radial position, due to cleavage of initiator as the fluid traverses the disk. These radicals would then propagate new chains and act to increase the overall reaction rate of the system. Work is continuing to assess whether this postulation can explain the rapid rates of polymerization achievable when using a SDR. As it has been found that shear cannot affect the rate of bimolecular termination, work is now continuing to assess how flow divergence and centrifugal extensions interact with polymerization kinetics.

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