Classical Cationic Polymerization of Styrene in a Spinning Disc Reactor Using Silica-Supported BF₃ Catalyst

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ABSTRACT: The carbo-cationic polymerization of styrene has been studied in a Spinning Disc Reactor (SDR) and the results were compared to those observed in a conventional Stirred Tank Reactor (STR). Addition of styrene to a slurry of silica-supported boron trifluoride (BF₃/SiO₂) in 1,2-dichloroethane led to uncontrollable reactions in the STR at monomer concentrations > 25%w/w and initial temperatures of 20–25°C. By comparison, monomer concentrations of 75% w/w were safely and controllably polymerized in the SDR at 40°C to yield polymers with molecular weights comparable to those reported in the literature for polymer prepared at −60°C. Exceptional heat transfer rates achieved in the SDR are sufficient to deal with the heat evolved when styrene is polymerized at concentrations as high as 75% w/w, the reaction proceeding under essentially isothermal conditions. In the present study, the effects of monomer/solvent feed rates, monomer concentrations, disc size, and disc speed on monomer conversions, polymer molecular weights, and polydispersities achieved in the SDR are investigated. Speculative explanations of the observed results are presented in terms of enhanced mixing effects on the polymerization mechanisms in the SDR. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 8–19, 2006

Key words: cationic polymerization; spinning disc reactor; silica-supported boron trifluoride; intensified heat transfer; polystyrene

INTRODUCTION

Cationic polymerization has been carried out since the early 19th century. There are many examples of styrene reacting violently with compounds such as concentrated sulfuric acid (H_2SO_4), boron trifluoride (BF_3), and stannic tetrachloride ($SnCl_4$) to give a product similar to that obtained when styrene was exposed to sunlight.[1] However, it was not until 1935 that the mechanism was elucidated when Whitmore showed that carbenium ions were involved.[2]

Classical cationic polymerization is an industrially used procedure that produces about 3 million tons of polymers per annum, this figure representing 3% of all industrially produced synthetic polymers.[3] However large volumes of chlorinated organic solvents, as well as hazardous acids such as aluminum chloride as catalysts, are used in the process, neither of which are environmentally friendly. A procedure that could significantly reduce, or even eliminate the use of these solvents and catalysts would result in a greener process and constitute a considerable advance in technology.

In terms of polymerization rate, the cationic mechanism gives propagation rate constants k_p in the range 10^4–10^6 L mol^{-1} s^{-1}, which are higher than those obtained by the free-radical mechanism (10^2–10^4 L mol^{-1} s^{-1}).[4] Consequently, conventional cationic polymerization is characterized by its uncontrollable nature, the result of a significantly more rapid rate of polymerization than free-radical polymerization. It is also far more susceptible to moisture and impurities as the active carbo-cations are much less stable than their free-radical counterparts, and are far more prone to undergo transfer and side reactions. As a result there is much less control over molecular weight and polydispersity than is available in free-radical polymerization. Chemical methods to control the cationic mechanism so as to give a "living" character to the polymerization have been developed and successfully introduced by Kennedy[5] and Sawamoto,[6] but only at the expense of reducing the rate of polymerization to levels at or below that of free-radical processes. Furthermore, such methods are currently limited to specialty polymer production.[5]

In a recent review of ionic polymerizations, Kennedy foresaw a renaissance of research into "clas-
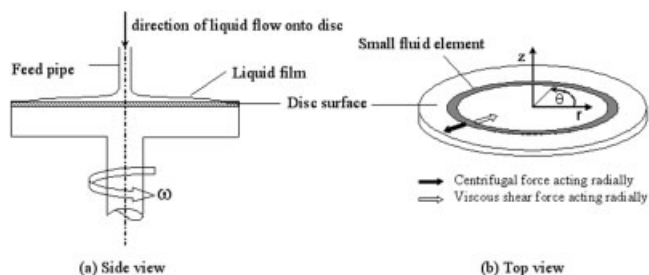
Figure 1 Thin film flow on spinning disc surface.

sical" cationic polymerization,[7] considering that acids or salts having noncoordinating counter ions e.g., $B\text{-}(C_6F_5)_4^-$ might be used to control polymerization in conventional batch reactors. From an engineering perspective, we believe that similar control of cationic polymerization may also be achieved by adopting novel approaches to reactor designs which incorporate intensified mixing and heat transfer. One such reactor technology is the spinning disc reactor (SDR).

Spinning disc reactor

The SDR is an intensified continuous reactor technology developed as part of the Process Intensification activities at Newcastle University. The centrifugal force generated on the horizontal disc surface as it rotates causes liquids fed to the center of the disc to flow as thin, highly sheared films within which conditions of very efficient heat transfer and mass transfer have been shown to prevail.[8–10] In this environment, highly exothermic fast reactions may be carried out in isothermal conditions even at ambient operating temperatures.

The cylindrical coordinates applicable to the thin film flow on the spinning disc surface are shown in Figure 1. A greatly simplified analysis of the hydrodynamic behavior of the film is provided by the "centrifugal model" derived from Navier–Stokes equations.[11] The basis of the centrifugal model is a balance between the centrifugal force and the opposing viscous force in the radial direction:

$$-\omega^2 r = \nu \frac{\partial^2 v_r}{\partial z^2} \qquad (1)$$

Various parameters for flow on the spinning disc surface have been derived previously on the basis of the centrifugal model. Selected parameters of interest to the present study are expressed as follows[11]:

$$v_r = \frac{\omega^2 r}{\nu}\left(\delta z - \frac{z^2}{2}\right) \qquad (2)$$

$$\delta = \left(\frac{3}{2\pi}\frac{\nu Q}{\omega^2 r^2}\right)^{1/3} \qquad (3)$$

$$t_{res} = \left(\frac{81\pi^2\nu}{16\omega^2 Q^2}\right)^{1/3}(r_o^{4/3} - r_i^{4/3}) \qquad (4)$$

$$\dot{\gamma}_{ave} = \frac{dv_r}{dz}\bigg|_{z=0} = \frac{\omega^2 r\delta}{2\nu} = 1.5\left(\frac{Q\omega^4 r}{18\pi\nu^2}\right)^{1/3} \qquad (5)$$

More complex hydrodynamic models, which are outside the scope of the present study, have been presented to describe flow on the rotating disc taking into consideration, for instance, the Coriolis acceleration in the angular direction.[10]

The present investigation involves a comparison of the performance of the SDR with that of a conventional stirred tank reactor (STR) for the heterogeneous cationic polymerization of styrene. A solid Lewis acid catalyst (BF_3 supported on silica) recently developed by the Green Chemistry Group at York University[12] was used to initiate the polymerization. Such catalysts can offer many advantages compared with their homogeneous counterparts[13,14]: ease of separation from the reaction mixture by filtration, mild reaction conditions, less harm to the environment, and possible reuse of the catalyst. Furthermore, the elimination of the water-quenching step—needed in homogeneous system at the end of the reaction to neutralize the Lewis acid—reduces the production of hazardous acidic waste. However, to the best of our knowledge, recent reported work on the use of solid acid catalysts has been rather limited.[15–17]

The SDR parameters of interest in this study were the disc residence time t_{res} and the average shear rate $\dot{\gamma}_{ave}$ as expressed in eqs. (4) and (5) respectively. The mean residence time represents the contact time between the various reacting species on the rotating disc while the average shear rate characterizes the degree of mixing achieved in the reacting film. As will be seen later, both parameters have a strong influence on the conversion of styrene observed in the SDR. These parameters were varied by changing the feed flow rate, the disc diameter, and disc speed. In addition, the effects of monomer concentration on styrene conversion and polymer molecular weight properties were investigated in the SDR. The performance of the SDR was compared with that of a conventional STR in which effects of monomer concentration, temperature control methods, and catalyst concentration were studied. In the experiments reported herein, the catalyst was used in the form of a slurry in 1,2-dichloroethane. We have also developed a system whereby the supported catalyst particles have been fixed onto the SDR reaction surface for a more environmentally friendly polymerization method; the results of this latter study will be reported in a future publication.

Figure 3 Expanded view of rotating chamber (shaded section in Fig. 2) showing internal heat transfer system of the SDR.

EXPERIMENTAL

Materials

Styrene (Aldrich, Dorset, UK 99%) was purified by passing through a 15-cm column of activated basic alumina, then drying overnight with anhydrous magnesium sulfate in a dark bottle. 1,2-dichloroethane (DCE) (Aldrich, Dorset, UK) was dried as received in the same manner as the styrene.

The boron trifluoride (BF_3) supported on silica (BF_3/SiO_2) (4 mmol/g loading) was prepared using established techniques.[12] Boron trifluoride dihydrate, $BF_3 \cdot (H_2O)_2$ (8.31 g, 80 mmol) was added to methanol (100 mL) in a 250 mL 3-neck round-bottom flask equipped with a reflux condenser and a magnetic stir bar. The support material (20 g of Kieselgel K100 (Merck, Dorset, UK), pretreated at 473 K for a minimum of 18 h) was added and the resulting slurry was stirred at 293 K under N_2 atmosphere for 2.5 h. The solvent was then evaporated under high vacuum (Schlenk line) at room temperature for a minimum of 15 h. The catalyst was further dried in Schlenk flasks on a high vacuum line prior to each use.

Apparatus

SDR

A schematic of the SDR used in this study is shown in Figure 2. It consists of a chamber enclosed in a water-cooled housing. The chamber is located on a double pipe rotating shaft driven by an electric motor so that the whole chamber arrangement spins around. The top surface of the rotating chamber is the reaction surface made of a 3 mm thick smooth stainless steel disc. The temperature of the reaction surface is controlled by a continuous flow of water through a narrow channel underneath it (Fig. 3). The water is pumped from a temperature-controlled water bath up the central shaft pipe into the channel in the chamber and it is returned to the bath through the outer shaft
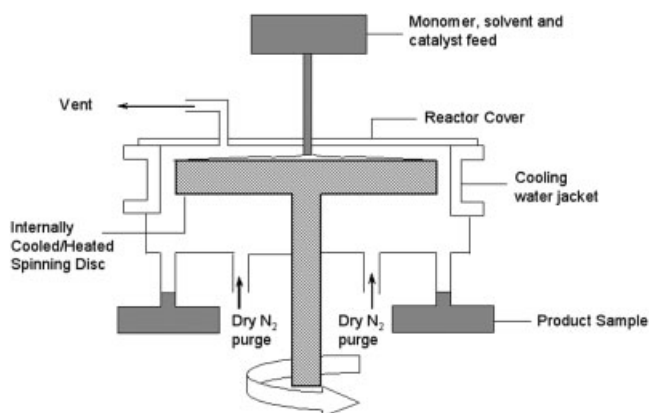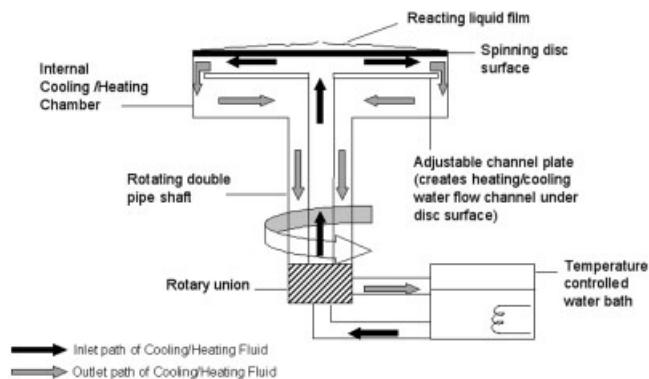
pipe. The disc housing has provisions for dry nitrogen inlets and product outlet tubes. The lid of the housing accommodates a feed inlet pipe directed to the center of the rotating disc and a vent for nitrogen exit.

After the monomer and suspended catalyst feeds are delivered to the center of the disc surface at known flow rates, the reacting mixture spreads on the rotating disc as a thin film and is rapidly thrown off to the edge of the disc after a residence time of the order of seconds. Two SDR units were used in our experiments: a small SDR having a 100 mm disc surface and a larger reactor with a 200 mm diameter disc.

Stirred tank reactor

Batch polymerizations were conducted in 500 mL flat-bottom flasks fitted with three neck adaptors. A double surface reflux condenser was attached to one neck, a thermocouple to another while the third served as an addition port, which was blanked off during the reaction. Stirring was achieved with a small bar magnet. Controlled temperature experiments were performed by either cooling in an ice bath or having water from a thermostatically controlled bath recirculating around the flask.

Procedure

SDR polymerizations

The desired amount of catalyst was added to DCE in a flask. The supported catalyst containing 4 mmol BF_3 per gram of catalyst was used at a concentration of 5% w/w based on the weight of styrene in all SDR runs. This concentration represents 1.3% w/w of BF_3 active sites. The catalyst was maintained in suspension in the DCE by continuous magnetic stirring. Purified and dried styrene was added to a second flask. Water from the controlled temperature bath was pumped through the SDR to bring the disc up to the chosen temperature of operation. The reactor was purged for about 15 min with dry

Figure 2 Schematic of SDR.
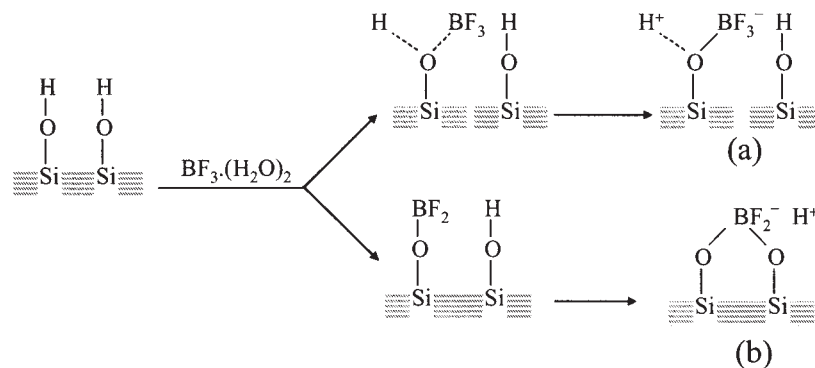
Scheme 1

nitrogen. The motor to the disc was then started up and the rotational speed was set to the required value on the digital speed controller unit. The selected rotational speed for the 100 mm disc was 200 rpm in all the runs while the 200 mm disc was operated at 400 rpm.

The styrene and BF$_3$/DCE suspension from the two flasks were pumped into a Y-piece mixer simultaneously at flow rates selected to give the desired combination of monomer concentrations and total feed flow rates. The mixture then flowed through a 4 m long PTFE tubing in the premix section prior to feeding onto the rotating disc to overcome the induction period of about 20–30 s typically observed in the batch polymerizations. A sample was collected from the end of the premix tube prior to introducing the feed into the SDR. After one pass on the rotating disc, the polymer product was collected and filtered to remove catalyst before its preparation for analysis.

STR polymerizations

The desired quantity of DCE was placed in the flask and stirred while the supported catalyst was added. The styrene was then added and the temperature of the reactants noted. Samples of the polymerizing mixture were taken at minute intervals up to the maximum temperature achieved in the run. The samples were filtered through a plug of glass wool and prepared for analysis.

Sample characterization

Samples were analyzed for conversion and molecular weights using a Gel Permeation Chromatography (GPC) set-up. Molecular weights were measured against narrow polystyrene standards (Polymer Labs, Church Stretton, UK).

In some cases conversion was also obtained by precipitation of the polymer with methanol. A 25 g sample of the reaction mixture was added to 250–300 mL of methanol. The polymer precipitate was filtered on a tared sintered glass funnel then washed three times

with methanol (25 mL each). The polymer was dried to constant weight in an oven at 75°C.

RESULTS AND DISCUSSION

It is important to understand the mechanism of the cationic polymerization of styrene to interpret the results from this study. Three consecutive reaction steps are generally involved: initiation, propagation, and termination.[18]

The grafting of BF$_3$ onto silica yields two possible structures for the Lewis acid-active centers, which initiate the cationic polymerization of styrene (Scheme 1).[17,19]

The proton generated from either process step in Scheme 1 attacks the double bond in the styrene molecule to form a monomer carbenium ion in the initiation stage (Scheme 2).

The polymer chain propagates by successive addition of monomer molecules to the active center (Scheme 3).

Termination of a propagating chain in cationic polymerization may take place via a number of reactions[18,20] including combination with the counterion, if the latter is sufficiently reactive, and transfer reactions with various species producing new active centers. Chain transfer to monomer by β-proton abstraction represents the most frequent transfer reaction in cationic alkene polymerizations resulting in an unsaturated polymer and a new monomer carbenium ion, which may start a new chain (Scheme 4).
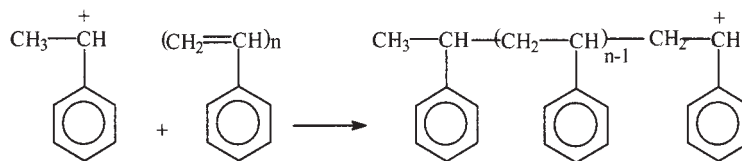
SDR slurry polymerizations

The effects of styrene concentration [St], feed flow rates, disc diameter, and disc speed on conversion and
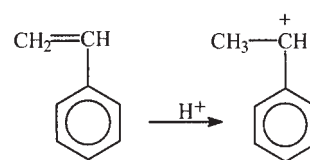
Scheme 2

Scheme 3

molecular weight properties were investigated in the SDR for the cationic polymerization of styrene using BF_3/SiO_2 suspended in DCE.
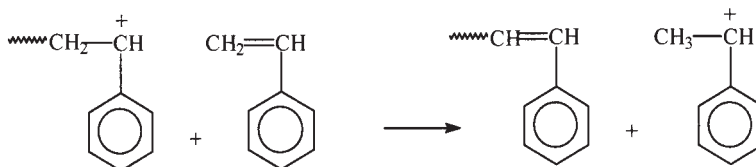
Effect of [st] and feed flow rate

It is observed that an optimum flow rate of 0.6 mL/s exists at the given set of conditions, whereby a maximum increase in conversion of about 8% is obtained in one disc pass (Fig. 4), with a corresponding average rate of polymerization of 8% per second based on a disc residence time of about 1 s (Fig. 5). This applies to both 49 and 75% w/w [St] in DCE. The change in monomer concentration does not appear to influence the conversion and polymerization rate greatly especially beyond the optimum flow rate. This seems to indicate that the polymerization rate is close to zero order with respect to [St] when the reaction occurs on the rotating disc. This is in sharp contrast to conventional cationic polymerization kinetics operating under assumed steady state conditions where the rate of polymerization is typically first or second order with respect to monomer concentration, depending on the rate determining step in the initiation process and the transfer reaction.[18] However, it has been reported that in systems with weak Lewis acids and nonpolar solvents, very strong complexation of active sites by monomer, followed by slow unimolecular rearrangement to generate carbenium ions from dormant species may lead to zero order kinetics in monomer.[21] It has also been suggested[20] that zero-order dependence on monomer may be observed in systems where the rate-controlling step in the initiation process is the initial formation of protons (Scheme 1) rather than the subsequent step of monomer attack by the proton in Scheme 2. We will see later that the latter explanation has greater validity for the SDR system. Also, it is possible that polymerization in the SDR proceeds under nonsteady state conditions where concentration of

carbenium ions never quite reaches a constant value during the short disc residence time of the order of seconds. Under such conditions, steady state polymerization kinetics would not be applicable and the dependence of the rate of polymerization on the monomer concentration may therefore not follow predictions based on steady state conditions.

The presence of an optimum flow rate as observed in Figures 4 and 5 may be explained by the opposing effects of decreased mean disc residence time t_{res} and increased mixing intensity as the flow rate is increased. As seen in eqs. (4) and (5), t_{res} is proportional to $Q^{-2/3}$ while the average shear rate, which characterizes the mixing intensity within the film, is proportional to the flow rate $Q^{1/3}$. These relationships are more clearly illustrated in Figure 6. It is observed from Figure 6 that average film shear rate increases with flow rate Q resulting in an increased mixing intensity between the supported catalyst and the styrene monomer molecules. At the same time, the residence time on the rotating disc (or the contact time between the catalyst and monomer molecules on the disc) decreases sharply as the flow rate is increased.

From Figures 4 and 6, it may be inferred that conversion is shear rate dependent (i.e., mixing intensity dependent) up until the optimum flow rate is reached. Thus we see a rise in SDR conversion with flow rate in the range 0.2 mL/s $\leq$ Q $\leq$ 0.6 mL/s, a trend that follows the increase in shear rate with flow rate. Beyond the optimum flow rate, the observed decrease in conversion is consistent with the decrease in t_{res}, indicating that t_{res} then becomes more influential than the shear rate. It is seen from Figure 6 that, at the optimum flow rate of 0.6 mL/s, a mean residence time of around 1 s is achieved on the disc surface. These results seem to suggest that, in the range of SDR conditions studied, a minimum disc residence time of about 1 s is required for the catalyzed polymerization to proceed at a rate dependent solely on the mixing
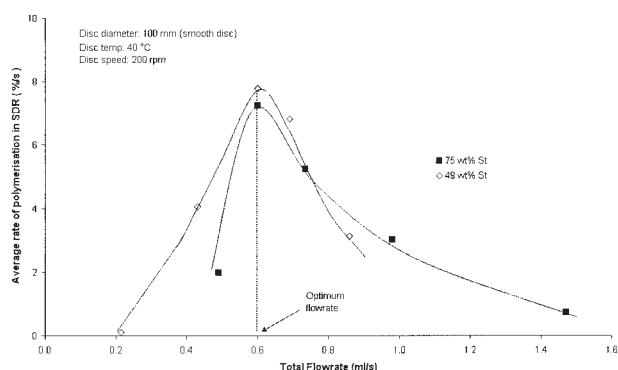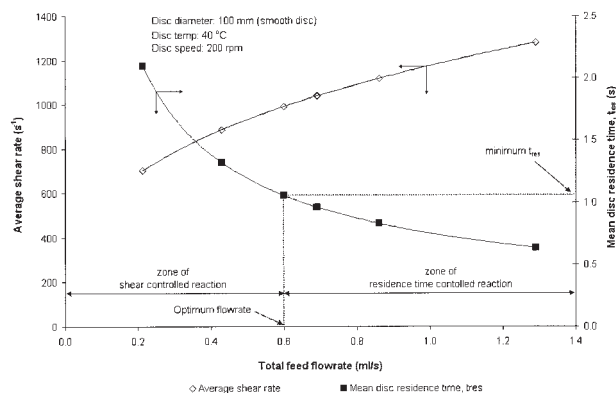

Scheme 4
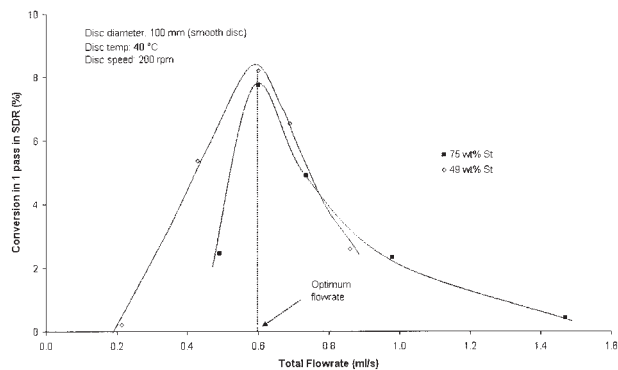
Figure 4 Effect of total feed flow rate on conversion in one disc pass in SDR using 49% w/w and 75% w/w styrene concentration.

Figure 6 Effect of total feed flow rate on calculated average film shear rate and mean disc residence time using 100-mm diameter disc rotating at 200 rpm.

intensity. This may indicate that an induction period of 1 s is needed for further activation of the Lewis acid catalyst on the disc surface. When the disc residence time exceeds the catalyst activation time, the reaction becomes shear rate or mixing controlled whereby higher shear rates enhance monomer diffusion through the pores of the silica support to the active catalyst sites, giving higher conversion levels. Mixing limitations are typical of reactions with extremely fast kinetics. The rate constant of propagation k_p for styrene and its derivatives polymerized by cationic mechanism is of the order of 10^5–10^6 L mol^{-1} s^{-1} at 0°C,[20] indicating the polymerization is a characteristically fast reaction and is therefore expected to be subject to the observed mixing dependencies.

Negligible influence of flow rate or monomer concentration on molecular weight properties was observed. For the range of flow rates considered, the polymer formed in the SDR had M_n and M_w in the range 20,000–30,000 g/mol and 25,000–45,000 g/mol respectively, with polydispersity indices (PDI) in the range 1.2–2.0. At the optimum flow rate of 0.6 mL/s giving a conversion increment of about 8% in one disc

Figure 5 Effect of total feed flow rate on average rate of polymerization in SDR using 49% w/w and 75% w/w styrene concentration.

pass (equivalent to 1 s reaction time), M_n and M_w were 25,000 g/mol and 37,000 g/mol respectively, with PDI of 1.5. These values are indicative of the control of molecular weight properties which can be achieved in the spinning disc environment. We believe that the added flexibility of short (1–5 s) and controllable residence times in the SDR is important for achieving control of such rapid reactions even at a higher operating temperatures of 40°C. Such tight control of residence times in batch reactors would be difficult to implement even with the most sophisticated control techniques, whereas the SDR has an inherent control mechanism by virtue of its processing capabilities.

Effect of disc diameter and disc speed

The effects of disc diameter and disc speed on conversion and molecular weight properties were evaluated using reactors having 100-mm and 200-mm discs operated at 200 rpm and 400 rpm respectively.

Changes in disc diameter and disc rotation speed affect both the mean disc residence time t_{res} and the average film shear rate, $\dot{\gamma}_{ave}$ as seen from eqs. (4) and (5) and Figure 7. Increases in disc diameter from 100 mm to 200 mm and disc speed from 200 rpm to 400 rpm more than doubles the shear rate over the range of flow rates considered. There is also a 60% increase in the disc residence time t_{res} on the larger disc rotating at a faster rate. If, as noted earlier, a minimum disc residence time of 1 s is required for conversion to be shear rate controlled, then, theoretically from Figure 7, the optimum flow rate would be expected to be close to 1.4 mL/s for the larger disc spinning at 400 rpm.

The effect of increasing disc diameter on the experimental conversion achieved in SDR is shown in Figure 8. An optimum flow rate is apparent on the larger disc in the range 1.25–1.6 mL/s, which is in agreement with the theoretical optimum value predicted in Figure 7 on the basis of the minimum mean residence

time requirement of 1 s. These data further reinforce the previous suggestion that an induction period of around 1 s is required before the catalyst can interact with the monomer effectively after introduction into the SDR environment. Once again, the optimum flow rate is indicative of the opposing effects of residence time and shear rates as discussed earlier.

It is also observed from Figure 8 that higher conversions are generally achieved on the larger disc at almost all flow rates tested, except for the very low flow rates. The combined effects of increased residence time and increased shear rate on the larger disc would be conducive to achieving higher conversions by providing longer time for reaction and a more vigorous and favorable mixing environment for the reacting species. Our observations lead us to predict that a much larger disc, say 1 m in diameter and rotating at speeds higher than 400 rpm, may provide enough residence time and high enough shear rates for much higher conversions to be achieved in a single pass on the rotating surface. Alternatively, a multi-pass arrangement in a reactor with a small disc surface coated with a layer of catalyst may not only permit efficient re-use of catalyst but also increase conversion significantly, as indicated by our preliminary results of such experiments which are currently underway.

A slight decrease in average M_n from about 21,000 g/mol to about 18,000 g/mol is obtained as the disc size increases from 100 mm to 200 mm diameter with a corresponding increase in PDI from 1.2–1.6 to 1.4–1.6 respectively. These changes may be due to the monomer/catalyst slurry fed to the disc at ambient temperatures being at the operating disc temperature of 40°C for longer on the larger disc, thereby increasing the probability of transfer reactions. This is discussed in greater depth in the section dealing with the heat transfer analysis of the SDR.

Stirred tank reactor polymerizations

To benchmark the performance of the spinning disc reactor for the BF_3/SiO_2 catalyzed cationic polymer-
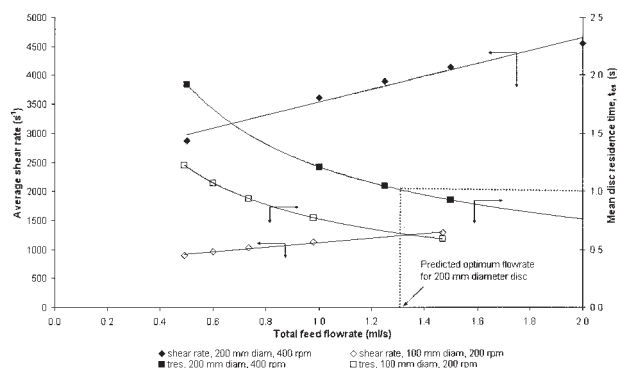
Figure 7 Effect of disc diameter and disc rotation speed on average shear rate and mean disc residence time t_{res} over a range of feed flow rates.
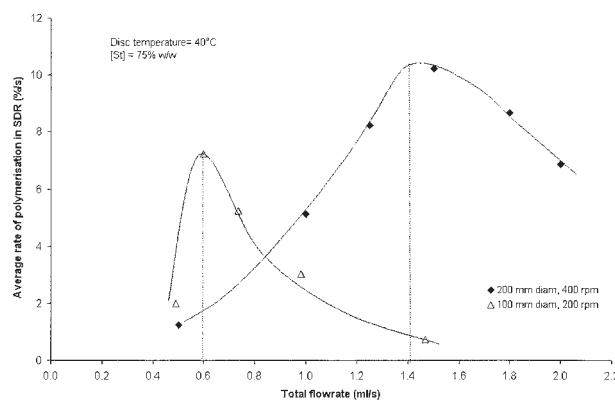
Figure 8 Effect of flow rate on experimental change in conversion in SDR using 100 mm and 200 mm diameter discs rotating at 200 rpm and 400 rpm respectively.

ization of styrene, runs were performed in a stirred batch reactor as described earlier. The effects of styrene and catalyst concentrations and of various temperature control systems on the polymerization were assessed. The range of conditions used is given in Table I. Selected temperature and conversion profiles are plotted in Figures 9 and 10 respectively, and molecular weight properties are compared in Table II.

It is evident from Figures 9 and 10 that rapid polymerization rates were accompanied by large, often uncontrollable exotherms. As expected higher styrene and BF_3 concentrations resulted in more rapid polymerization rates. Adequate control of the reaction is achieved by limiting the monomer concentration to about 25% w/w in the solvent with a conventional water bath kept at room temperature. At 49% w/w [St], control of the polymerization is readily lost if the reaction system is not cooled to low temperatures of < 10°C (Runs B4 and B5). This inevitably results in low polymerization rates (10% conversion after 30 min in Run B4). We noted that there was a sudden surge in the temperature in Run B5 once the reaction temperature reached around 30°C after about 1 h (not shown on Fig. 9) whereby the temperature rapidly rose to 99°C, giving a final yield of 80%. Therefore cooling the reaction mixture at the start of the reaction only helps to delay the exotherm rather than control it.

The benefits of having a constant temperature bath around the batch vessel at either 20°C or 40°C rather than carrying out the reaction adiabatically did not materialize for high concentrations of styrene in DCE (49% w/w). We still observed a rapid loss in control of the polymerization at this concentration for both Runs B8 and B9. It is clear from these experiments that conventional cooling systems, such as recirculating cooling water, are extremely inefficient in controlling reaction temperatures in the rapid and highly exothermic cationic polymerization of styrene in a batch vessel at high monomer concentrations and ambient starting temperatures.

TABLE I
Conditions for Batch Slurry Polymerization Runs

Run	[Styrene] (% w/w)	[BF$_3$] (% w/w)	Temperature control method during polymerization	Temperature at start, T_s (°C)	Maximum temperature reached (°C)
B1	18	2.6	None	21.4	63.0
B2	18	1.3	None	24.0	56.0
B3	49	1.3	None	22.0	88.4
B4	49	1.3	Ice bath at 7°C	21.5	21.5
B5	49	1.3	None	7.0	99.0 (after 1 h reaction time)
B6	24	1.3	Water bath at 40°C	38.5	46.5
B7	24	1.3	Water bath at 20°C	20.4	21.6
B8	49	1.3	Water bath at 40°C	36.0	97.0
B9	49	1.3	Water bath at 20°C	21.2	95.8

At high styrene concentration, higher molecular weights were obtained at lower operating temperatures in runs B4 and B5 (with corresponding lower conversions) where transfer and hence chain termination are reduced. Corresponding PDIs were in the range 1.5–2.0. However, in systems with large, uncontrollable exotherms (Runs B3, B8, B9), molecular weights were low and PDIs were greater than 3.0. These PDIs are within the range expected for classical cationic polymerization systems in conventional stirred vessels.[22–24] It is worth noting that, within the range of conditions investigated using the stirred tank reactor, living or controlled polymerization would be difficult to achieve due to the low micromixing levels (slow initiation) and high transfer rates.

In an ideal cationic polymerization system where transfer reactions are absent, it is expected that polymer molecular weights increase linearly with conversion.[22] However, strong deviations from ideal behavior are observed at higher temperatures due to the increasing influence of chain transfer reactions on the growing chain. Our conversion and molecular weight data for runs B3, B4, and B5 in Table II clearly demonstrate such deviations. In run B3 where the polymerization was allowed to proceed adiabatically at initial ambient temperature of 22°C, a high uncontrol-

lable rate of polymerization (giving a conversion of 91% in 10 min) was observed under conditions of increasing polymerization temperature resulting from the large reaction exotherm associated with styrene polymerization. These effects are clearly illustrated in Figures 9 and 10. The large temperature rise causes a dramatic increase of the rate chain transfer which explains the lower molecular weights and broader MWD at the high conversion. We believe both transfer to monomer and intramolecular transfer, which is more significant at low monomer concentrations, would be the main transfer mechanisms. On the other hand, runs B4 and B5 proceeded almost isothermally at ambient temperature yielding low conversion and high molecular weight polymer. These observations are in agreement with Pepper's analysis[22] of the influence of temperature on chain transfer and molecular weights for the carbo-cationic polymerization of styrene by perchloric acid.

Our results clearly indicate that control of the temperature and therefore the rate of the polymerization in the STR are critically important if desirable molecular weight properties such as high molecular weights and low PDI are to be obtained. High concentrations of environmentally harmful solvents generally have to
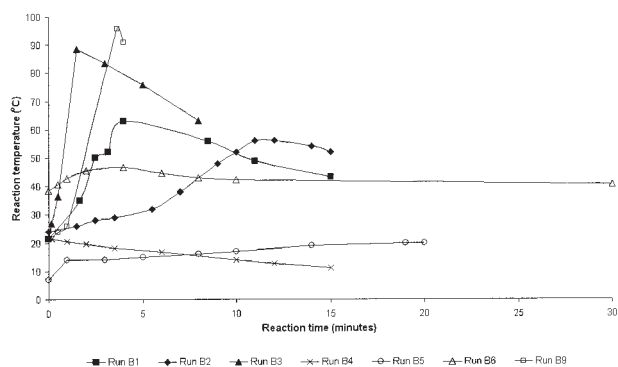
Figure 9 Temperature profiles in batch slurry cationic polymerization of styrene.
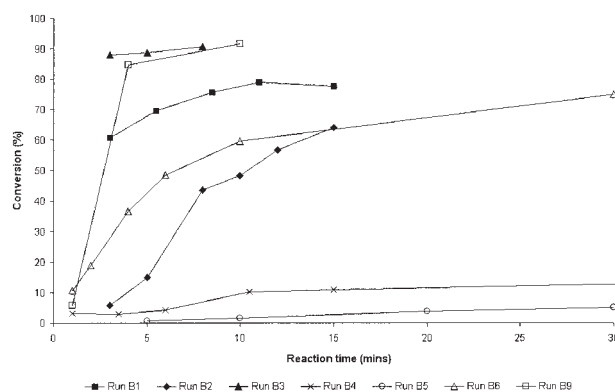
Figure 10 Conversion profiles for batch slurry cationic polymerization of styrene.

TABLE II
Molecular Weight Properties of Final Polymer Product from Batch Slurry Polymerization Runs

Run	[Styrene] (% w/w)	[BF$_3$] (% w/w)	Conversion (%)	M_n	PDI
B1	18	2.6	78	5199	3.3
B2	18	1.3	64	9956	1.9
B3	49	1.3	91	4098	3.3
B4	49	1.3	13	12032	2.0
B5	49	1.3	5[a]	13857[a]	1.4[a]
			98[b]	4631[b]	2.9[b]
B6	24	1.3	75	10568	2.0
B7	24	1.3	5	17054	1.7
B8	49	1.3	94	4100	3.1
B9	49	1.3	92	4389	3.2

[a] 30 min into polymerization (before exotherm).
[b] 3 h into polymerization (after exotherm).

be used to give dilute monomer solutions which, combined with ice-cooled reaction conditions, give slow but fairly controllable polymerization rates. However, in performing the polymerization at a slow rate in the heat transfer limited stirred vessel, the reaction time is inevitably extended. An ideal reactor system should enable the cationic polymerization of styrene to proceed at its inherently fast rate while being able to cope effectively with the large amounts of heat rapidly generated. The SDR offers all the characteristics of such a reactor.

Continuous SDR versus batch STR

The SDR and batch polymerization data are compared in Table III. It is clearly difficult to control the polymerization in the batch at about 50% w/w [St] while maintaining the water bath around the vessel at 40°C (Run B8). The reaction spirals out of control giving a maximum temperature of 97°C within 1 min into the reaction. This also has a detrimental effect on the molecular weights and polydispersity of the polymer formed. It is therefore important to cool the batch to very low temperatures at the expense of low rates of

polymerizations as seen in Run B5. On the other hand, controlled operation at the elevated temperature of 40°C using 49% w/w [St] is possible in the SDR which gives a higher average rate of polymerization and higher molecular weights (Run S14) than the cooled batch at 17°C (Run B5). The SDR has also been shown to be capable of handling styrene concentrations up to 75% w/w in a safe and controllable manner with good control of molecular weight distributions (Runs S21, S26, S31). A higher disc temperature of 40°C allows reactions to proceed faster (Run S26) than at 20°C (Run S31) at the expense of slightly lower but reasonable molecular weights.

We believe that these improvements in the cationic polymerization of styrene in the SDR even at high temperatures and high monomer concentrations may be due to a combination of factors such as the high heat transfer rates from the polymerizing thin film, the short and easily controllable residence times (1–5 s) of the reaction mixture on the rotating disc and the dynamics of the thin film. With enhanced heat transfer, safe operation at high temperatures to give higher rates of polymerization is feasible. Previous studies have indicated that vigorous micromixing conditions exist within the thin film on the rotating disc.[25–27] We believe that such a highly intense mixing environment applied to the heterogeneous cationic polymerization of styrene may be responsible for the observed control in polydispersity achieved in the SDR. An increase in proton-monomer interactions according to Scheme 2 is likely in the SDR, resulting in an enhancement of the initiation reaction and in a higher concentration of styryl carbenium ions than would be found under batch reactor conditions. This would also explain the apparent zero order of polymerization rate on styrene concentration since an enhancement in reaction shown in Scheme 2 may result in the ionization step in Scheme 1 becoming the rate controlling step in the initiation process and the rate of initiation R_i being independent of styrene concentration. Thus, if steady state conditions apply (where $R_i = R_t$), the rate of polymerization R_p may also become independent of

TABLE III
Cationic Polymerization in Batch and SDR Using 1.3 wt % BF$_3$ Suspended in DCE

Reactor type	Run no.	[St] (% w/w)	Reaction Temp. (°C)	Residence time (s)	Conversion (%)	Ave. rate of conversion (%/s)	M_n	PDI
Batch	B5	49	17	360	4.1	0.0114	14902	1.48
			41	4200	10	0.0024	12710	1.84
Batch	B8	49	97	60	94	1.57	4100	3.12
SDR	S14[a]	49	40	1.0	7.6	7.6	24679	1.68
SDR	S21[a]	75	40	1.1	7.8	7.1	25050	1.46
SDR	S26[b]	75	40	0.9	9.5	10.6	14593	1.60
SDR	S31[b]	75	20	1.0	4.1	4.1	17045	1.73

[a] Disc diameter= 100 mm; disc speed= 200 rpm; flowrate= 0.7 mL/s.
[b] Disc diameter = 200 mm; disc speed = 400 rpm; flowrate= 1.5 mL/s.

styrene concentration if termination proceeds exclusively by transfer to monomer (Scheme 4). The corresponding kinetic expressions for the stipulated reactions are shown in eqs. (6)–(9)

$$R_i = k_i[BF_3/SiO_2] \tag{6}$$

$$R_p = k_p[M^+][M] \tag{7}$$

$$R_t = k_{tr,M}[M^+][M] \tag{8}$$

If $R_i = R_t$, eq. (7) becomes

$$R_p = \frac{k_p k_i[BF_3/SiO_2]}{k_{tr,M}} \tag{9}$$

However, the observed low polydispersities of the polymer from the SDR also suggest that initiation rate and polymerization rate may be of the same order of magnitude. Under the centrifugal forces and plug-flow conditions prevailing on the rotating disc, the growing polymer chains may be extended and favorably oriented such that the active chain ends are easily accessible for monomer addition (Scheme 3) resulting in enhanced propagation rates R_p. It may well be that propagation dominates over transfer to monomer (Scheme 4) in the SDR environment even at ambient temperatures, as evidenced by the higher molecular weights and lower polydispersities of the SDR polymer (Table III) than would be achieved in a batch process under comparable temperature conditions. Indeed, data reported by Plesch[28] for the cationic polymerization of styrene using $TiCl_4$ as Lewis acid initiator indicate that molecular weights of ~6000 and 20,000 g/mol could only be achieved at extremely low temperatures of $-25°C$ and $-60°C$ respectively. This is further evidence that transfer in the SDR environment at ambient temperatures is suppressed to levels as low as those at $-60°C$ in conventional systems. Thus, although eq. (9) would explain the zero order dependence of R_p on monomer concentration, it may not be applicable in the SDR since the high molecular weights in the SDR suggest that termination by transfer rate, R_t, is much lower than the initiation rate R_i.

Heat transfer characteristics of SDR

The excellent heat transfer characteristics of the SDR play a major role in controlling the cationic polymerization of styrene. In this section, we provide an analysis of the heat transfer system of the SDR in an attempt to demonstrate the extent to which good temperature control can be achieved in the thin film on the rotating surface.

The heat transfer system of the SDR is shown diagrammatically in Figure 11. During cooling of the
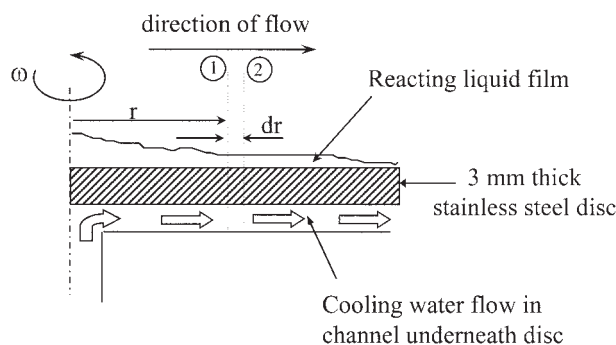

Figure 11 Heat transfer across rotating disc surface.

process fluid on the SDR surface, heat is transferred across the stainless steel disc from process liquid film to the cooling water in the underside channel. As an approximation, the system is assumed to behave as a parallel flow single pass heat exchanger.

To assess the effect of the enhanced heat transfer achievable in the SDR on the cationic polymerization of styrene, the temperature profile of the thin reacting liquid film flowing across the rotating disc surface may be calculated from a heat balance. A simple heat balance on a small annular element of liquid film of width dr at a radial distance r from the center of the disc (i.e., between sections 1 and 2 shown in Fig. 11) is given by:

Rate of heat change = Heat released by polymerization reaction - Heat removed by cooling water

$$mc_p dT_f = \frac{2\pi r dr(\Delta H_r)}{\pi(r_o^2 - r_i^2)} - 2\pi r dr h_o(T_f - T_d) \tag{10}$$

The derivation and application of the eq. (10) is subject to the following simplifying assumptions:

1. Heat transfer occurs mainly by convection from the liquid film to the disc surface in a direction perpendicular to the plane surface of the disc.
2. The thickness of the film is considered to be so small and mixing within the film is so intense that temperature variations across the height of the film are assumed to be negligible. Only temperature differences in the radial direction are significant.
3. The temperature of the disc surface T_d remains constant in the radial direction due to the relatively large mass of metal involved in the heat transfer process in comparison with the fluid mass.
4. The average film heat transfer coefficient h_o over the entire disc surface is taken to be constant at 10 kW/m² K from previously reported work.[8]
5. Conversion and heat of reaction liberated change linearly in the radial direction with disc surface area available for reaction.

Numerical integration of eq. (10) yields the temperature profile of the liquid film on the disc surface as shown in Figures 12 and 13 for different disc surface temperatures. In computing these profiles, total heat of reaction released, ΔH_r, corresponding to a given monomer conversion X% achieved per disc pass is calculated from:

$$\Delta H_r = \Delta H_{poly} Q V \rho_{st} X \qquad (11)$$

where the heat of polymerization for styrene, ΔH_{poly}, is taken as 702 kJ/kg (equivalent to 73 kJ/mol of styrene).[24]

Conversions of 50% have been used in the simulation to assess the impact on heat transfer rates and film temperature control of a large amount of heat being released at high conversions. It is seen in Figures 12 and 13 that the liquid film fed to the disc at ambient initial temperature quickly reaches the temperature of the disc surface and remains close to that temperature as it flows and polymerizes across the disc surface. These results clearly demonstrate the ability of the SDR to tightly regulate the temperature of the processed fluid by its significantly enhanced heat transfer rates. This is crucial to achieving the control in polymer properties.

CONCLUSIONS

As an intensified reactor technology, the SDR offers many potential benefits in its application to classical cationic polymerization systems. The intense mixing characteristics and enhanced heat rates achieved in the thin films make the SDR an ideal reactor for performing such fast, highly exothermic reactions which require rapid mixing and an efficient heat removal system.

This present study has demonstrated that the mean disc residence time and the average film shear
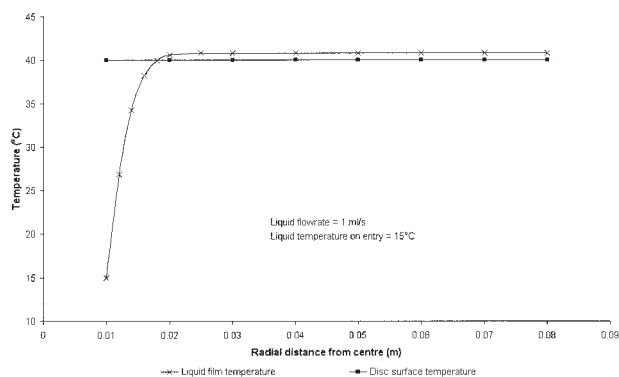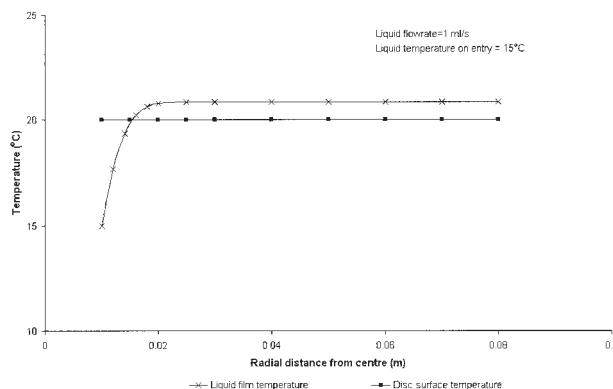
Figure 13 Reacting liquid film temperature profile with disc surface temperature T_d at 20°C

rate are the most influential parameters in determining the level of conversion in the cationic polymerization of styrene using a silica-supported BF_3 catalyst in slurry form. An increase in conversion of about 10% has been achieved in a mean disc residence time of about 1 s, with the film subjected to an average shear rate of 4100 s^{-1} on a 200-mm diameter disc rotating at 400 rpm. To achieve higher conversions, larger residence times (> 1 s) combined with higher shear rates would be needed. Both requirements may be fulfilled by using a much larger disc optimized for feed flow rate and disc speed.

We have also shown that in a conventional stirred batch reactor where heat transfer is generally poor and where the cationic polymerization of styrene proceeds in an approximately adiabatic fashion, monomer concentrations of 25% w/w are the maximum if uncontrollable exotherms are to be avoided. By comparison, one pass on the spinning disc allows the use of 75% w/w of styrene which polymerizes in an essentially isothermal manner, even at the relatively high temperature of 40°C, to give a polymer having molecular weight and polydispersity equal to, or better, than those given at ca.20% w/w in a stirred reactor. Clearly the reduction in solvent usage in the SDR is significant. Enhancements in the rates of initiation and propagation coupled with the possible extension and favorable orientation of growing chains in the centrifugal field environment are believed to be responsible for the observed low polymer polydispersities (<2.0) in the SDR. Transfer to monomer in the SDR also appears to be suppressed in comparison to propagation as indicated by the relatively high molecular weights ($M_n >$ 15,000 at 40°C). The enhanced heat transfer rates in the SDR give better temperature control in the polymerizing film and allow near to isothermal reaction conditions for improved control of polymer molecular weight properties.

Figure 12 Reacting liquid film temperature profile with disc surface temperature T_d at 40°C

NOMENCLATURE

Description

c_p specific heat capacity of fluid [J kg^{-1}K^{-1}]

h_o film heat transfer coefficient on rotating disc surface [W m^{-2} K^{-1}]

ΔH_{poly} heat of polymerization [J/kg]

ΔH_r heat released by polymerization in one disc pass [W]

k_i initiation rate constant [s^{-1}]

k_p propagation rate constant [L mol^{-1} s^{-1}]

$k_{\text{tr, }M}$ rate constant for transfer to monomer [L mol^{-1} s^{-1}]

m liquid mass flow rate [kg/s]

M_n number average molecular weight [g/mol]

M_w weight average molecular weight [g/mol]

MWD molecular weight distribution

N disc rotational speed [rpm]

PDI polydispersity index

Q volumetric flow rate [m^3/s]

r radial distance from center of disc [m]

R_i Rate of initiation [mol L^{-1} s^{-1}]

R_p Rate of polymerization [mol L^{-1} s^{-1}]

St styrene

T temperature [K]

t_{res} mean residence time [s]

V Initial volume fraction of monomer in feed

v_r radial velocity [m/s]

X Fractional monomer conversion

z vertical distance along the z-axis [m]

Greek symbols

δ film thickness [m]

$\dot{\gamma}_{ave}$ average shear rate [s^{-1}]

η dynamic viscosity [Ns/m^2]

ν kinematic viscosity [m^2 s^{-1}]

ρ density [kg/m^3]

ω angular velocity (= $2\pi N/60$) [rad/s]

Subscripts

d disc

f fluid on disc surface

i disc inlet

o disc outlet

st styrene

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