Bulk Free-Radical Polymerization of Styrene on a Spinning Disc Reactor

M. R. Moghbeli, S. Mohammadi, S. M. Alavi

School of Chemical Engineering, Iran University of Science and Technology, P.O. Box 16844-13114, Tehran, Iran

ABSTRACT: The bulk free-radical polymerization of styrene was carried out on a spinning disc reactor (SDR) with prepolymer feeds previously prepared in a stirred batch reactor at 70°C. The SDR significantly enhanced the reaction rate when the conversion of the prepolymer feed was about 50%. There was an optimal disc rotation speed, that is, 1500 rpm, at which the conversion enhancement was maximized. Increasing the disc rotation speed up to 1500 rpm increased the conversion, but a further increase beyond this speed caused the conversion enhancement to decrease. This behavior could be attributed to the dual effect of the disc speed (controlling both the residence time and the effective radial mixing of the reaction media) on the disc. On the other hand, the multipass disc feeding mode was used as an approach to increase the residence time and evolution of the conversion of the reacting mixture in the SDR. Surprisingly, a maximum conversion change of about 40% was achieved for a prepolymer feed of 50% after three passes across the rotating disc. Furthermore, the effect of multipass disc feeding on the molecular characteristics of the SDR products was investigated. In comparison with the results obtained at a feed conversion of 30%, the weight-average molecular weight, the *z*-average molecular weight, and the polydispersity index of the three-pass SDR products prepared with a 50% feed conversion at a rotation speed of 1500 rpm were lower than those of the one-pass products. This behavior could be attributed to probable chain scission of long polymer chains as a result of the high shear and elongation forces that arose on the disc surface. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 709–715, 2009

Key words: polystyrene; radical polymerization; thin films

INTRODUCTION

Free-radical polymerization methods are widely applied to commercial monomers such as styrene, acrylics, vinyls, and their mixtures, both by research scientists and in industry, to produce polymers with various desirable properties. It is well known that two general free-radical solution and suspension methods for the polymerization of styrene have most commonly been used to manufacture polystyrene, as opposed to the bulk method, which produce products of much higher purity. The limitation of mass transfer and heat removal from bulk polymerization reactors, which arises from the significant viscosity enhancement, especially at higher monomer conversions, decreases the performance of this polymerization method in producing commercial high-quality products in comparison with the aforementioned methods.[1] Even though the gel effect substantially increases the polymerization rate during the course of bulk polymerization, the increased viscosity leads to a poor degree of mixing and a broadening of the molecular weight distribution.

Recently, new polymerization reactor technology has been developed that allows the generation of extremely high mass-transport and heat-transport rates in the reactor.[1–5] This new technology greatly increases the free-radical polymerization rate and consequently reduces the polymerization process time. Polymerization reactions of a few vinyl monomers such as styrene, butyl acrylate, methyl methacrylate, and unsaturated esters have been performed in thin, highly sheared films with a spinning disc reactor (SDR).[1–8] The results have shown that SDR technology is suitable for performing reactions that are heat-limited and mass-limited and for enhancing the polymerization rate without a significant change in the polydispersity of the polymer product.[1,9] In fact, the rotation of a disc provides excellent micromixing and film homogeneity and elongates the reacting fluid elements over the disc surface because of axial acceleration.[1,9,10]

To understand the phenomena that take place on the spinning disc surface, kinetic/mechanistic studies of free-radical polymerization in an SDR have been carried out.[10–12] There is a belief that the centrifugal forces and divergent nature of the reacting

film on the spinning disc provide conditions that tend to minimize the termination of the macroradicals, and as a result, the polymerization rate is greatly increased.[11] In another scenario, which is envisaged on the basis of the very low residence time of reaction media on the rotating disc surface, an equilibrium radical concentration is not achievable, and an increased radical population in the reaction medium leads to an enhanced polymerization rate.[11]

Although a number of research studies have been carried out to assess the effectiveness of SDR technology for the solution free-radical polymerization of some vinyl monomers,[1–3,6–12] less attention has been paid to the performance of bulk free-radical polymerizations in an SDR. In this research, the bulk free-radical polymerization of styrene was carried out on a rotating disc surface at 70°C with 2,2-azobisisobutyronitrile (AIBN) as the initiator. The effects of some polymerization process parameters, such as the initiator content, prepolymer feed conversion, rotational disc speed, and multipass disc feeding, on the SDR product conversion and molecular weights were investigated.

EXPERIMENTAL

Materials

All reagents were purchased from Merck Co. (Darmstadt, Germany) unless otherwise stated. Styrene was distilled *in vacuo* and stored at 0–5°C before use. AIBN, used as an initiator, was first recrystallized from methanol. The solvent, high-performance-liquid-chromatography-grade tetrahydrofuran, was also used for molecular weight determination.

Bulk polymerization of styrene

The bulk free-radical polymerization of styrene was carried out in two stages; the first stage involved prepolymer feed preparation in a stirred batch reactor, and in the second stage, the polymerization was continued in an SDR. The synthesis of the prepolymer feed was carried out in a 200-mL glass reactor equipped with a reflux condenser, a nitrogen inlet, and a septum through which samples were taken for kinetic analysis. The polymerization was conducted in a batch process under thermostatic control and was continued for 140 min. The reaction mixture was maintained at 70°C and was stirred at 300 rpm under a nitrogen atmosphere. The prepolymer feeds, with various overall conversions ranging from 30 to 56 wt %, were prepared by the adjustment of the polymerization reaction time. The AIBN initiator contents used in the batch polymerization were 0.5,
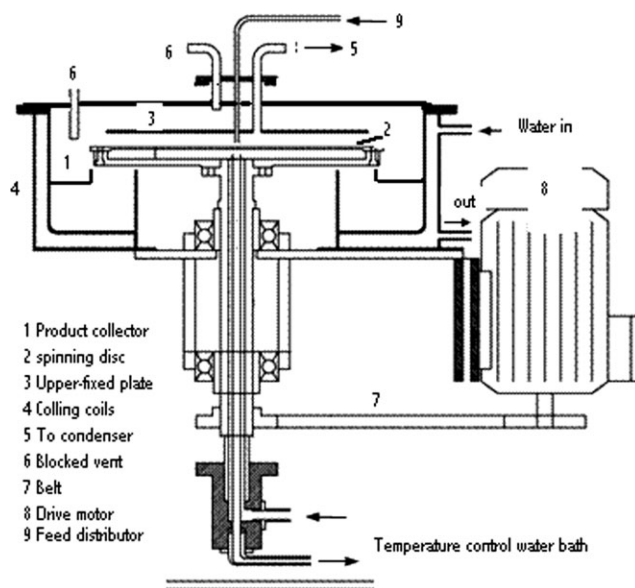

Figure 1 Schematic of the SDR.

1, and 2 wt % with respect to the total amount of the monomer.

The SDR used in this study consisted of a spinning disc surface, a prepolymer feed distributor, a product collector, a steel reactor enclosure, and cooling coils. The rotating disc was made of 316 stainless steel with a smooth surface, and it was 200 mm in diameter. The spinning disc surface and its associated parts were placed in a stainless steel enclosure capped by a flat-glass top section to enable direct visual observation of the reacting liquid flowing across the spinning disc surface (Fig. 1). The prepolymer was fed into the SDR through a glass pipe that extended downward from the feeder and was positioned just above the disc surface at a radial distance of about 25 mm from the center of the disc. The product generated on the disc was thrown off the hot surface and crashed into the cool surrounding steel wall, whereupon it was collected in the collector for use in further studies.

Multipass disc feeding

After a given initial prepolymer feed was passed and it was thrown off the disc surface, the product was cooled by circulating water in the reactor wall to prevent further polymerization. This one-pass SDR product was then used as a new SDR feed to continue the bulk polymerization over the disc surface under polymerization conditions similar to those of the previous step. In this case, the new SDR feed, collected after each disc pass, was preheated to 50°C before use in the next feeding process. In a similar manner, the two-pass SDR feed was used to produce a three-pass SDR product.
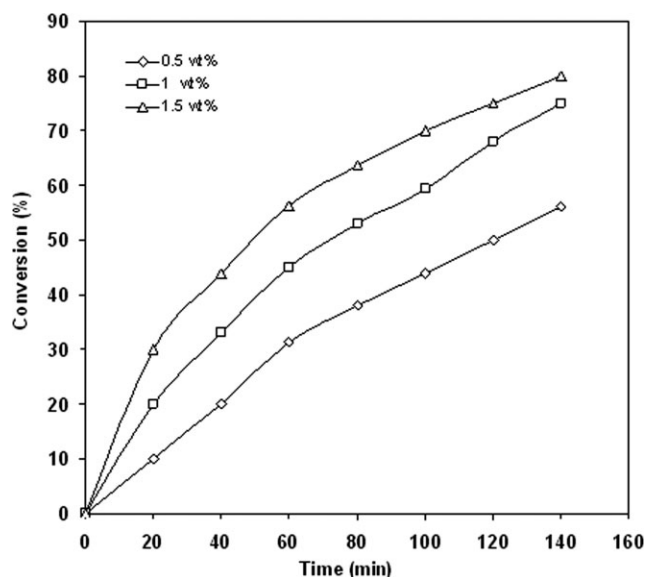
Figure 2 Time dependence of the evolution of the conversion for the batch polymerization of styrene with various initiator levels at 70°C.

Kinetic study

Samples (1 mL) of the prepolymer feeds were taken from the reaction mixture in the batch reactor at different polymerization times and poured into aluminum dishes cooled in an ice–water mixture. The dishes were placed in a vacuum oven at 25°C for 24 h. The evolution of the weight conversion versus time was measured gravimetrically. A similar method was used to measure the SDR product conversion. As soon as the disc was stopped, three cooled product samples were taken from the collector for conversion measurements.

Molecular weight determination

The molecular weights and molecular weight distributions of both the batch and SDR products were measured with a gel permeation chromatography (GPC) apparatus (Shimadzu, Tokyo, Japan) equipped with a refractive-index detector. Dilute polystyrene solutions were injected into the GPC column (Waters Corp., Milford, MA; 10^4 Å). The temperature of the column was 40°C.

RESULTS AND DISCUSSION

Prepolymer preparation

The prepolymer feeds with various conversions required for the second-stage polymerization in the SDR were prepared in a batch polymerization process at 70°C. Figure 2 indicates the conversion behavior with time in the batch polymerization using various initiator concentrations ranging from 0.5 to 1.5 wt %. As can be seen, increasing the initia-

tor content led to a steady increase in the conversion rate because of the increase in the radical concentration as a result of more extensive decomposition of the initiator. At a higher initiator concentration, there was no significant mixing problem even at higher monomer conversions up to 80%, but beyond this conversion, the viscosity and elasticity of the melt prepolymer were increased considerably. According to Figure 2, the bulk polymerization of styrene was continued for the appropriate reaction times to generate feeds having the predetermined conversion levels.

SDR polymerization

Effect of the prepolymer feed conversion

For the second-stage polymerization, the prepolymer feeds prepared with AIBN (1 wt %) as the initiator and having conversions in the range of 30–56% were fed onto the spinning disc surface at different spinning speeds ranging from 400 to 1500 rpm at a disc temperature of 70°C. The effect of the prepolymer feed conversion on the one-pass product conversion versus the disc rotation speed is shown in Figure 3. Obviously, an increase in the conversion of the SDR products was observed as the feed conversion and disc rotation speed were increased. Rather similar behavior of a uniform conversion enhancement with increasing disc speed was obtained for the lowest and highest feed conversions, whereas for intermediate feed conversions, a shift in the SDR product conversion at higher rotational speeds was observed. Although a higher disc rotation rate increased the
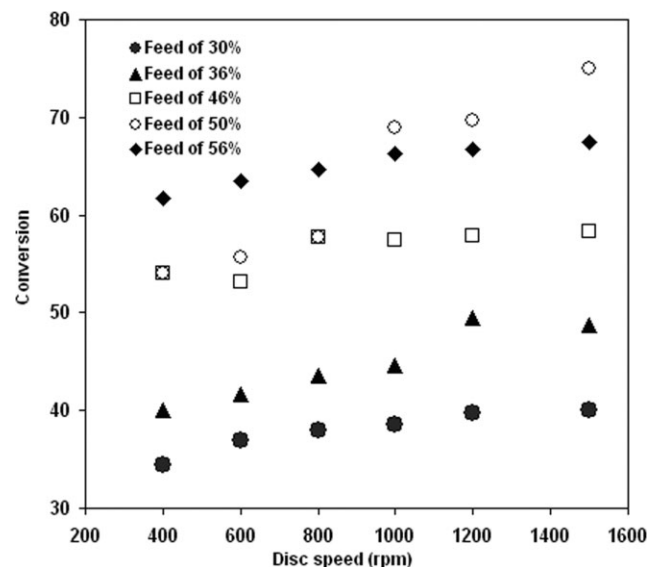

Figure 3 Effect of the disc speed on the SDR product conversion for prepolymer feeds with different conversions and a fixed initiator level of 1 wt %.
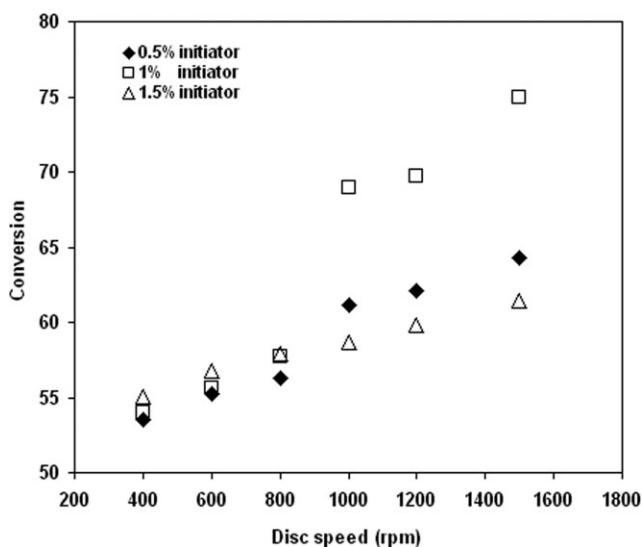
Figure 4 Effect of the initiator level on the SDR product conversion variation versus the disc rotation speed for a prepolymer feed of 50%.

axial acceleration and mixing efficiency in the reacting liquid film, it also reduced the residence time of the reacting liquid on the disc surface, especially for the prepolymers used with lower conversions. The highest conversion enhancement corresponded to a feed conversion of 50%. This enhancement implies that there is an optimum feed conversion and viscosity at which good radial micromixing and adequate residence time of the growing chain radicals on the rotating disc surface result in the highest conversion change. Using a higher feed conversion above 50% decreased the effective micromixing and radial chain alignment, both of which increased the polymerization rate. Applying feed conversions below 50% resulted in a shorter residence time on the spinning disc surface, thereby leading to a lower conversion enhancement.

Effect of the initiator content

Figure 4 shows the conversion enhancement of single-pass SDR products versus the disc speed for prepolymer feeds of 50% synthesized with 0.5, 1, or 1.5 wt % AIBN as the initiator. The conversion enhancement of the feed with an initiator concentration of 1.5 wt % rose uniformly with increasing disc speed. On the contrary, reducing the initiator content caused the SDR product conversion to increase considerably at a disc rotation speed of about 1000 rpm. Increasing the initiator content caused the transfer to the initiator to be the dominant transfer reaction, and consequently, the initiator efficiency was decreased. On the other hand, a higher radical population as a result of increasing initiator content in the polymerizing mixture on the disc may have

increased unfavorable recombination reactions between the radicals and thereby lowered the polymerization rate. Nevertheless, the highest conversion change was obtained with a prepolymer feed prepared with 1 wt % AIBN as the initiator (Fig. 4).

Effect of the disc rotation speed

The conversion in a single pass of the SDR was found to be a function of both the prepolymer conversion and the disc rotation speed. To quantitatively assess the effect of the disc rotation speed on the product conversion change, a prepolymer feed of 50% conversion prepared with a 1 wt % concentration of the initiator was fed onto the rotating disc surface at various rotation rates ranging from 400 to 2000 rpm. The maximum conversion enhancement of 25% in the SDR was observed at a disc speed of 1500 rpm. The conversion enhancement increased with increasing disc speed up to 1500 rpm, but at higher disc speeds, a decrease in the conversion change was observed. This behavior can be attributed to the dual effect of the disc rotation speed (controlling both the residence time and the effective radial mixing of the reaction medium) on the rotating disc surface. Although a higher disc rotation rate increased the axial acceleration and mixing efficiency in the reacting liquid film, it also reduced the residence time of the growing chain radicals on the disc surface, and this, in turn, lowered the polymerization rate. For disc speeds up to 1500 rpm, the efficient micromixing compensated for the lowering of the residence time as the disc speed increased. In contrast, increasing the disc speed above the optimum level remarkably reduced the residence time
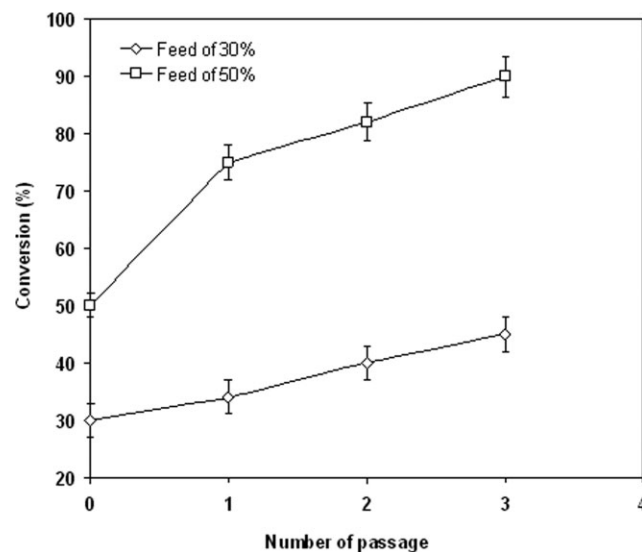

Figure 5 Effect of the multipass disc feeding mode on the SDR product conversion enhancement at a fixed rotation speed of 1500 rpm.
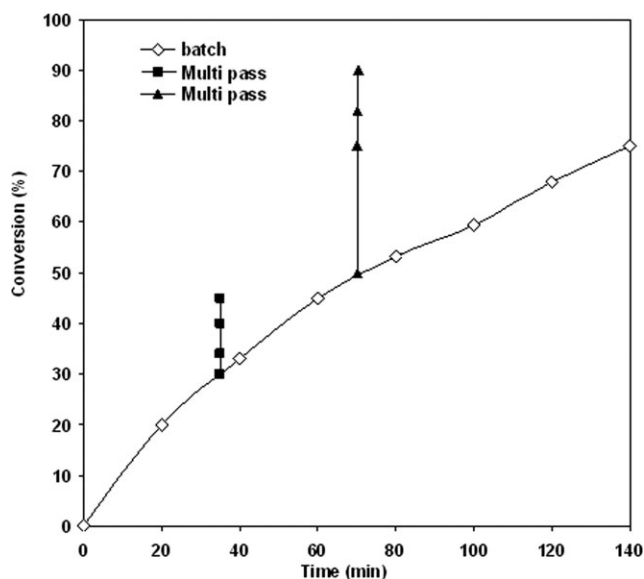
Figure 6 Comparison of the conversions in batch polymerization and multipass SDR at a fixed rotation speed of 1500 rpm.

and conversion enhancement of the reacting liquid on the disc surface.

Effect of multipass disc feeding

To increase the residence time and evolution of the conversion of the reacting mixture in the SDR, the prepolymer feeds were consecutively passed over the rotating disc surface three times. Thus, the one- and two-pass SDR products were used as new SDR feeds to continue the bulk polymerization on the rotating disc under the same polymerization conditions. Figure 5 indicates the conversion enhancement of one-, two-, and three-pass SDR products at a rotation speed of 1500 rpm with prepolymer feeds of 30 and 50% conversion. As can be seen, there was a considerable conversion enhancement in the multipass disc feeding mode. In other words, the polymerization on the SDR under these feeding

conditions could lead to considerable time savings in comparison with the conventional polymerization process conducted in a batch reactor (Fig. 6). As can be seen, in each disc-pass stage, a significant conversion enhancement was obtained during a very short reaction time in the SDR. Surprisingly, a maximum conversion change of about 40% was achieved for the prepolymer feed of 50% conversion after three passes of the rotating disc. Nevertheless, the polymerization rate in the second- and third-pass stages was lower than that in the first stage (Fig. 5). The high viscosity of the reaction media on the disc surface in the second- and third-pass stages may have adversely affected the effectiveness of the SDR in the bulk polymerization of styrene. However, the use a different initiator with a higher decomposition temperature or increasing the polymerization temperature may offer a means of overcoming this drawback arising in the multipass disc feeding mode. In contrast, for the low-viscosity prepolymer feed of 30%, a rather uniform polymerization rate increase was observed (Fig. 5).

Molecular weight changes in the SDR

Table I shows the effect of the multipass disc feeding mode on the molecular characteristics of the SDR products. The weight-average molecular weight (M_w) and polydispersity index (PDI) of the polystyrene in the prepolymer feed of 50% were increased with one pass of the SDR, whereas the number-average molecular weight (M_n) decreased. Thus, the new polymer chains added to the reaction mixture during passage over the rotating disc seemed to have a lower M_n value than the prepolymer feed chains (Table I and Fig. 7). On the other hand, increasing the disc speed from 1000 to 1500 rpm for the feed of 50% conversion did not significantly alter the molecular characteristics of the SDR products (Fig. 7). It should be mentioned that the observed small "flat" station in the middle of the molecular weight distribution curves can be related to the systematic error during measurements. Thus, the

TABLE I
Molecular Characteristics of the Batch and SDR Polymer Products

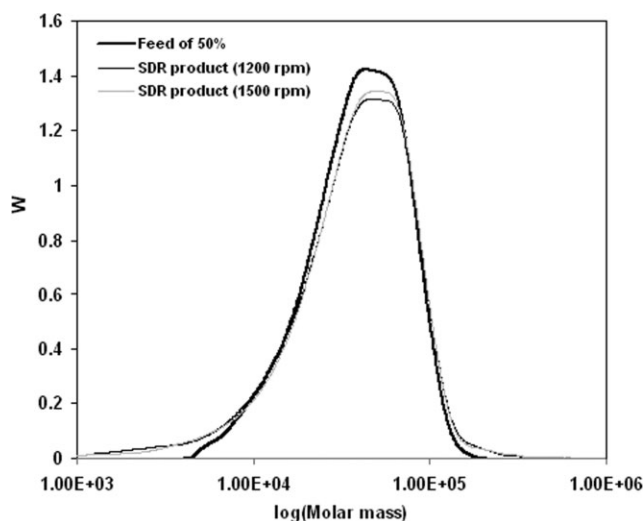| Sample	Overall conversion (%)	Rotating disc speed (rpm)	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	PDI
50% batch	50	—	30.2	45.4	60.5	1.50
One pass	60	1000	23.7	47.8	73.5	2.01
One pass	75	1500	23.3	47.0	69.1	2.02
Three passes	90	1500	27.2	45.3	62.0	1.67
30% batch	30	—	23.9	41.1	55.4	1.71
One pass	34	1500	23.7	40.5	54.9	1.70
Three passes	45	1500	24.3	44.4	51.0	1.82

Figure 7 Effect of the disc speed on the SDR product molecular weight distribution with a prepolymer feed of 50% W, normalized derivative.

obtained GPC results should be considered to have an error of ±5%. For the feed of 30 wt %, the molecular characteristics of the one-pass disc products were slightly inferior to those of the prepolymer feeds prepared in the batch polymerization system. This behavior can be attributed to the lower viscosity of the reaction media obtained with a lower feed conversion, which effectively suppressed the diffusion limitation of mass and heat transfer in the SDR.

Using one- or two-pass disc products as new, highly viscous prepolymer feeds for the next polymerization stage led to an increase in the residence times of the reaction media on the disc. Interestingly,
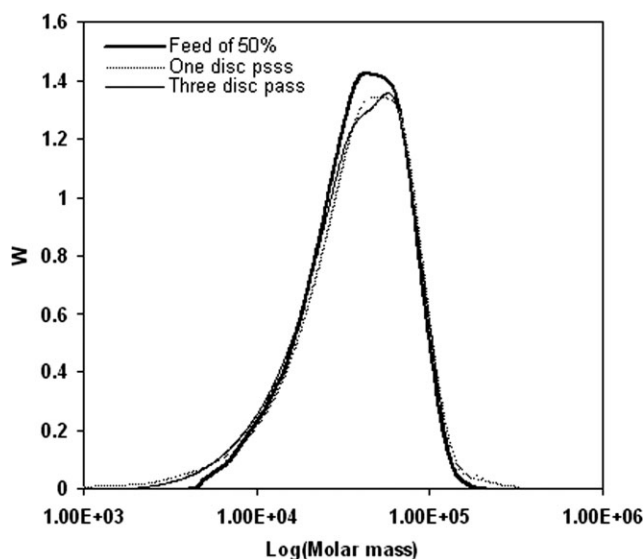

Figure 8 Effect of multipass disc feeding on the SDR product conversion at a fixed rotation speed of 1500 rpm (the initial feed conversion was 50%) W, normalized derivative.
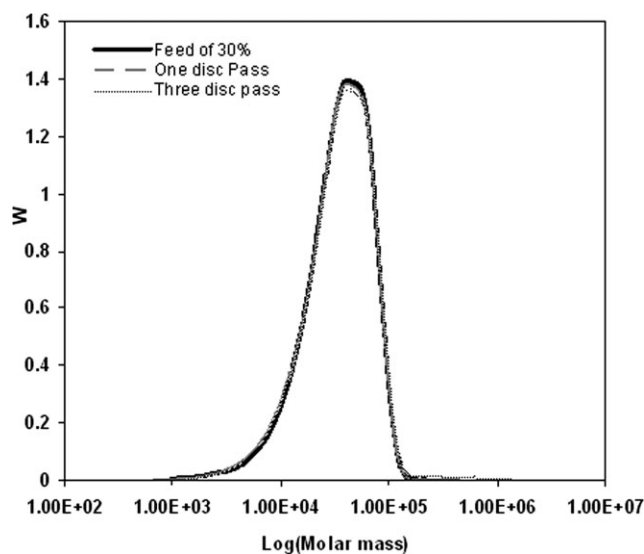

Figure 9 Effect of multipass disc feeding on the SDR product molecular weight distribution at a fixed rotation speed of 1500 rpm (the initial feed conversion was 30%) W, normalized derivative.

the PDI of the three-pass SDR product based on an initial feed of 50% with the highest viscosity was lower than that of the one-pass SDR product (Table I and Fig. 8). In this case, the decrease in the z-average molecular weight (M_z) of the three-pass SDR product in comparison with the one-pass product showed that with a higher viscosity of the reaction medium and with a greater shear force, the bigger polymer chains on the rotating disc could break up into shorter chains, thereby reducing the M_w and M_z values (Table I). In contrast, the opposite was true for the PDI and M_w values of the three-pass SDR product prepared with a prepolymer feed conversion of 30% (Table I and Fig. 9).

CONCLUSIONS

The bulk free-radical polymerization of styrene was carried out with an SDR with thermal initiation by AIBN at rotating disc speeds in the range of 400–1500 rpm and at a reaction temperature of 70°C. Analyzing the effect of the prepolymer feed conversion on the one-pass SDR product conversion showed that the highest conversion change was achieved when a 50% feed conversion prepolymer was used for the polymerization at 1500 rpm. In this case, the multipass disc feeding mode considerably increased the conversion enhancement, although M_w and M_z as well as PDI of the SDR products decreased slightly with an increasing number of disc passes. This behavior can most likely be attributed to chain scission of the long polymer chains influenced by the high shear/elongation forces in the SDR.

References

1. Boodhoo, K. V. K.; Jachuck, R. J. Appl Therm Eng 2000, 20, 1127.
2. Jachuck, R. J.; Ramshaw, C. Presented at the IChemE Research Event/First European Conference, Edinburgh, United Kingdom, 1995.
3. Boodhoo, K. V. K.; Dunk, W. A. E.; Jachuck, R. J. J Appl Polym Sci 2002, 85, 2283.
4. Cheong, S. I.; Choi, K. Y. J Appl Polym Sci 1995, 58, 1473.
5. Boodhoo, K. V. K.; Dunk, W. A. E.; Vicevic, M.; Jachuck, R. J.; Sage, V.; Macquarrie, D. J.; Clark, J. H. J Appl Polym Sci 2006, 101, 8.
6. Vicevic, M.; Novakovic, K.; Boodhoo, K. V. K.; Morris, A. J. Presented at the 17th International Congress of Chemical & Process Engineering, Prague, Czech Republic, 2006.
7. Boodhoo, K. V. K.; Dunk, W. A. E.; Jassim, M. S.; Jachuck, R. J. J Appl Polym Sci 2004, 91, 2079.
8. Boodhoo, K. V. K.; Jachuck, R. J. Green Chem 2000, 2, 235.
9. Vicevic, M.; Boodhoo, K. V. K.; Scott, K. Chem Eng J 2007, 43, 133.
10. Vicevic, M.; Novakovic, K.; Boodhoo, K. V. K.; Morris, A. J. Chem Eng J 2008, 135, 78.
11. Leveson, P.; Dunk, W. A. E.; Jachuck, R. J. J Appl Polym Sci 2003, 90, 693.
12. Vicevic, M.; Novakovic, K.; Boodhoo, K. V. K.; Morris, A. J. Presented at the Conference on Process Intensification and Process Innovation, Christchurch, New Zealand, 2006.