

# Influence of Centrifugal Field on Free-Radical Polymerization Kinetics

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**ABSTRACT:** It has been observed that when a prepolymer mix of styrene, poly(styrene), toluene, and benzoyl peroxide is transferred from a conventional stirred tank reactor (STR) to a spinning disc reactor (SDR), the rate of polymerization is substantially increased. Furthermore, the molecular weight and the molecular weight distribution of the polymer formed at conversions up to about 80% in the SDR is virtually unchanged from that of the polymer formed at 60% conversion in the STR. These results seem to indicate that the increase in polymerization rate is not the result of the well-known Trommsdorff–Norrish effect, which would be expected to lead to an increase in polydispersity. We believe that shear and centrifugal forces experienced by the film provide intense mixing and extension flow effects, which are responsible for the above-described observations. In this report an explanation has been put forward to describe the observed effects. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2283–2286, 2002

**Key words:** polydispersity; Trommsdorff–Norrish effect; free-radical polymerization; gel permeation chromatography; synthesis

## INTRODUCTION

Free-radical polymerization is the most important technique used industrially for the synthesis of addition polymers. The method is robust, thus allowing a wide choice of solvents, initiators, and conditions: only oxygen must be excluded from the reaction mixture. However, with the exception of emulsion polymerization, which proceeds by a unique mechanism, it is not possible to achieve high molecular weight while at the same time increasing the rate of polymerization.<sup>1</sup>

An approach to a technique that might allow substantial increases in polymerization rate, while maintaining high molecular weight, has been studied at the Process Intensification and

Innovation Center (PIIC) at Newcastle University. Utilizing a thin film reactor in the form of a spinning disc,<sup>2</sup> the free-radical polymerization of styrene has been carried out at rates of polymerization that are higher by orders of magnitude than those observed in conventional reactors. Furthermore, molecular weights and polydispersities have not been affected for polymers formed up to 80% conversion. The findings at Newcastle have generated significant industrial interest and a detailed program to understand the kinetics based on real-time process monitoring techniques is currently under way.

## EXPERIMENTAL

Styrene was polymerized at 90°C in a conventional stirred tank reactor (STR) using benzoyl peroxide as the free-radical initiator. Toluene

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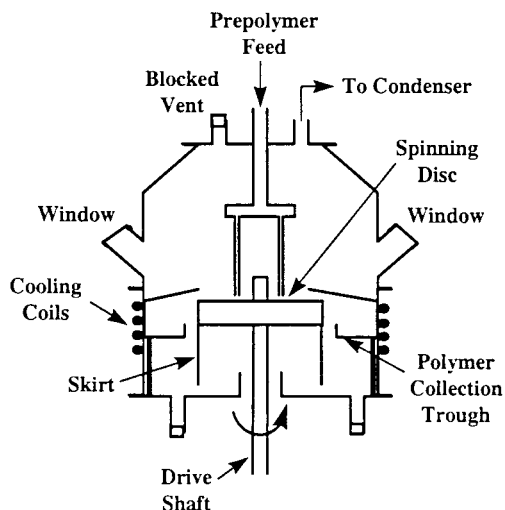


Figure 1 Schematic of SDR.

(10–15% v/v) was added to reduce viscosity. At 50–60% conversion the reaction mixture was pumped at the desired rate (18–54 kg/h) onto a grooved disc held at 90°C and rotating at speeds between 400 and 1200 rpm. A schematic of the reactor setup is shown in Figure 1. The main features were described in a previous publication.<sup>2</sup> The spinning disc reactor (SDR) feed and product samples were collected, quenched, and analyzed for conversion, molecular weight, and polydispersity using gel permeation chromatography (GPC) technique.

## RESULTS AND DISCUSSION

Increases in monomer conversion as high as about 20% have been achieved in one pass across the disc surface (Fig. 2), corresponding to a residence time of approximately 5 s. Samples of polymer taken from the SDR when conversion had reached about 80% were found to have molecular weights and polydispersities virtually identical to those found for the feed polymer at about 60% conversion. Typically, the polydispersity index was  $1.8 \pm 0.2$ . These results were reported in an earlier publication.<sup>2</sup>

As a tentative explanation of our results we utilized the rheological concept of shear thinning and extension flow. On the surface of the SDR, thin highly sheared polymerizing films are formed. These films (50–300  $\mu\text{m}$ ), shown in Figure 3, are associated with high mixing intensities, shear rates, and plug flow characteristics. Initially, the shear forces may lead to disentanglement of preformed inactive coiled chains, thus bringing about a reduction in the viscosity of the prepolymer mix by shear thinning, as depicted in Figure 4.<sup>3</sup> This effect would be more pronounced at higher polymer concentrations and molecular weights. As new polymer chains grow, they can be expected to experience a certain degree of extension as the polymerizing film travels radially outward under the influence of the centrifugal force, which increases proportionally with the radial

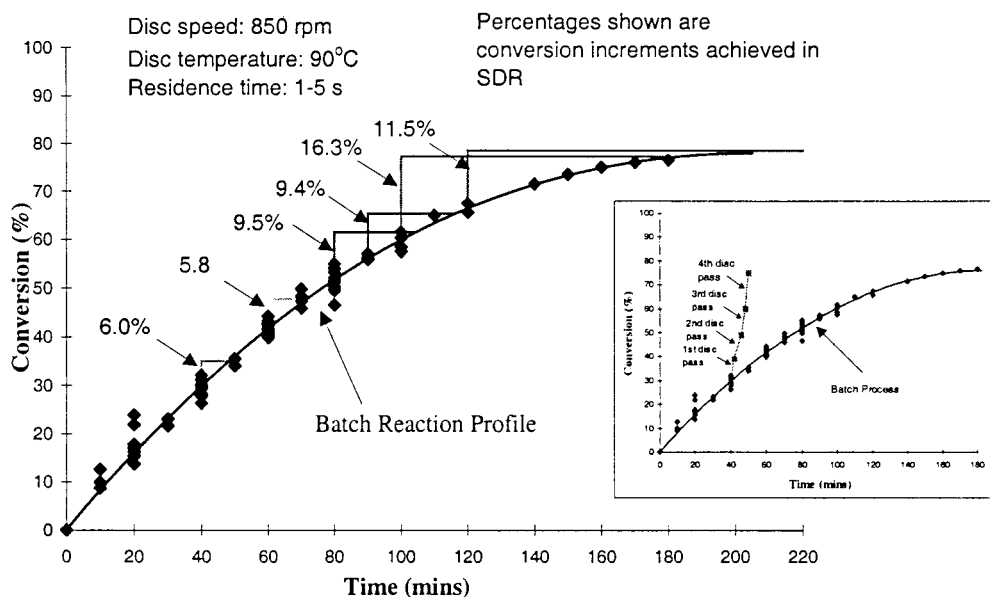
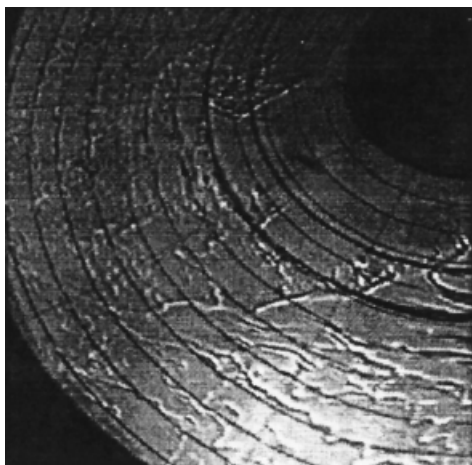


Figure 2 Plot comparing styrene polymerization in batch and SDR with inset depicting a proposed process with a cascade of discs rotating at 850 rpm.



**Figure 3** Surface waves on thin liquid films in SDR.

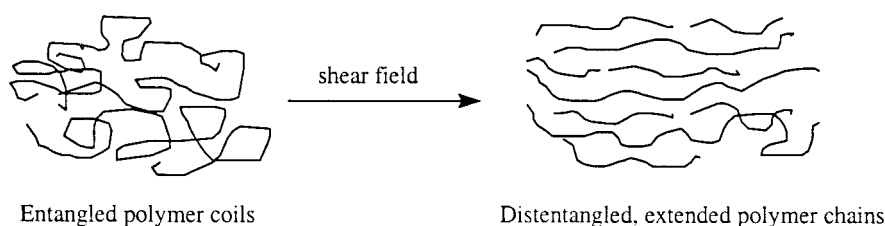
distance ( $F = \omega^2 r$ ). Also, it seems likely that the degree of extension would be dependent on the disc rotational speed, which is expected to influence the translational and segmental diffusion of active chains and, therefore, bimolecular termination reactions would be reduced. On the other hand, monomer molecules would find enhanced access to the active, propagating polymer chains rather in the manner of “living” systems. It is also thought that the lowering of viscosity by shear thinning and the excellent mixing characteristics in the thin film play important roles in maintaining high initiator efficiency, even at moderate to high monomer conversions. Thus if a high rate of initiation can be induced and sustained on the rotating disc while bimolecular termination is limited, then it is likely that non-steady-state conditions would prevail in the SDR, especially given that the residence time on the disc is comparable to the time to reach steady state ( $<5$  s). We believe that the kinetic chain length of the newly formed polymer chains is very similar to the length of those in the prepolymer.

Moreover, it seems plausible that, as the newly formed polymer chains are extended and are

growing radially, translational diffusion of the active chains becomes restricted. Segmental diffusion may similarly be affected, although possibly to a lesser extent, given that chain ends may be sufficiently mobile and accessible to other polymeric entities. Therefore, the overall termination rate constant  $k_t$  is reduced. This suggested decrease in termination between disentangled, extended polymer chains attributed to the physical forces acting on the rotating disc represents the opposite effect to that observed by Ludwico and Rosen.<sup>4</sup> Using dilatometry, the latter found that the polymerization rate fell as polymer–polymer interactions increased as a result of a shrinkage of dimensions of the polymer coils. Consequently, diffusion control effects on termination rate were reduced, with a subsequent increase in  $k_t$ .

Although it is as yet unproven, we believe that conditions on the spinning disc may contribute to a reduction in cage effects, which would normally result in low initiator efficiency. Under the shear thinning effect and high mixing intensities in the SDR, the efficiency of the initiator may be as high on the disc as it was at the start of the STR polymerization, such that the rate of initiation in the SDR is similar to that experienced at the start of the reaction. In the physical environment on the disc, the radially extended active polymer chains would be readily accessible to monomer molecules and in the short disc residence time, propagation might be likened to that seen in “living” systems, that is, where all chain-breaking reactions are suppressed.

The observation that molecular weight and polydispersity of polymer at 80% conversion from the SDR are relatively unchanged from those formed at 60% in the STR clearly indicates the influence of the physical environment in the SDR compared to that of the STR. An increase in polymerization rate achievable in the SDR without sacrificing molecular weight or polydispersity indicates that the gel effect, which is normally characterized by an uncontrolled increase in molecu-



**Figure 4** Effect of shear on polymer coils.<sup>3</sup>

lar weight, is suppressed in the SDR, the very short residence time probably playing a very important role.

At the present time, we are not clear as to the relative importance of termination reactions. Once the polymerizing film is not experiencing termination by free-radical and bimolecular termination between chains up to high conversion levels it seems to indicate that primary radical termination plays only a minor role in termination up to conversions of 80%, given that there is no significant change in polydispersity. The diminishing monomer concentration and relatively high availability of initiating radicals would, in conventional reactors, be expected to give low molecular weight polymers and an increase in polydispersity. Our observation of unchanged polydispersity in the SDR seems to indicate that polymer chains having a molecular weight below the critical value for entanglement are mobile enough to enter into bimolecular termination reactions with the active ends of extended, longer chains. Therefore a continuous process, such as the one involving the SDR, that gave reproducible polydispersities in the range 1.5–2.0, even at high conversions, would mark a considerable advance in the industrial production of polymers synthesized by the free-radical mechanism.

## CONCLUSIONS

Our results appear to demonstrate that it is possible to induce an acceleration in the polymerization of styrene without compromising either mo-

lecular weight or polydispersity by conducting the polymerization in a spinning disc reactor. The enhancement of rate is achieved in a safe and controllable manner, in sharp distinction to the autoacceleration observed in conventional reactors.

The use of continuous-feed reactors at high mass fractions of polymer is an industrial technique for conducting free-radical polymerizations in the Trommsdorff–Norrish region in a controllable way.<sup>5</sup> An example of this approach has been reported by Lau et al.<sup>6</sup> On the basis of our preliminary results we believe that a continuous process, such as the one involving the SDR, would mark a significant advance in the industrial production of polymers having polydispersities close to the theoretical limit in a controlled and reproducible manner. This technology is expected to offer opportunities for developing sustainable polymer processes using the concepts of process intensification.

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