

Numerical Investigation of Kinetics of Free-Radical Polymerization on Spinning Disk Reactor

P. Leveson, W. A. E. Dunk, R. J. Jachuck

Process Intensification & Innovation Centre, School for Chemical Engineering & Advanced Materials, University of Newcastle upon Tyne NE1 7RU, United Kingdom

Received 19 November 2002; accepted 27 January 2003

ABSTRACT: Spinning disk reactor (SDR) technology has been demonstrated to achieve significant enhancements in free radical polymerization rates. The effect on the rate may be attributed to the unique hydrodynamic environment experienced by the reacting polymer films. The rotating surface of a SDR promotes extension of the polymer chains, which may prevent the propagating chains from terminating through bimolecular reactions. In this article, a numerical simulation is performed to investigate how reduced rates of termination would affect time conversion behavior of free

radical initiated styrene polymerization. Comparisons have been made between model predictions and SDR experimental results. The closeness between predicted and experimental results yields strong evidence that the hydrodynamic regime created on the surface of a SDR can lead to reduced rates of bimolecular termination. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 693–699, 2003

Key words: spinning disk reactor (SDR); free radical polymerization; numerical simulation; styrene

INTRODUCTION

Spinning disk reactor (SDR) technology has been demonstrated to achieve significant enhancements in free-radical polymerization rates.¹ Rate enhancements by orders of magnitude have been experienced for both free-radical and condensation polymerizations.² This technology exploits the benefits of centrifugal force, which produces thin highly sheared films due to radial acceleration. The hydrodynamics of the film result in excellent fluid mixing and high heat, as well as mass transfer rates. These characteristics make it suitable for performing reactions that are heat and mass transfer limited, particularly where viscous fluids are involved. It is believed that the excellent mixing and plug flow characteristics should aid in producing polymer products characterized by tight molecular weight distributions.

To investigate the theory of polymerization on an SDR, a series of experiments using online FTIR and Raman techniques is currently being undertaken. We believe that utilizing these techniques will allow the measurement of a radial conversion profile from the SDR which will facilitate the development of a mechanistic model to describe the polymerization rates and molecular weight of products for a range of different feed and operating conditions.

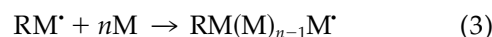
It has been proposed that, because of the unique hydrodynamic conditions on the disk, it is possible that terminations through bimolecular reactions are minimized because of a linear extension of the polymer chain.¹ In this article a theoretical model is developed to calculate propagation rates in the absence of termination reactions. Comparisons are then made between model predictions and experimental data. Before presenting our kinetic study, a brief review of the relevant chemistry is given.

Polymerization kinetics

The mechanisms for chemically initiated free-radical polymerization are well documented³; thus, only a brief 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 the 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).



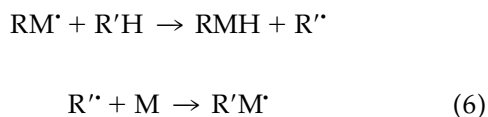
For each addition of monomer to the growing chain there is also a probability that the chain may undergo

Correspondence to: R. J. Jachuck (r.j.jachuck@ncl.ac.uk).

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



EXPERIMENTAL

Boodhoo et al.⁴ have conducted extensive studies into the rates of the polymerization of styrene in both batch reactors and SDRs. Their work quantified the rate enhancements observed when using an SDR and showed how the polydispersity of the SDR product remained constant, even beyond conversions where the gel effect would be expected to result in broadening of the weight distribution of the products.

The experiments were conducted with a feed mixture composed 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 it was then fed onto an SDR. The final product was quenched and then analyzed. Using this technique, both the time conversion behavior of the batch system and the SDR were measured.

The results of a series of batch runs are shown in Figure 1. Superimposed on Figure 1 is the time conversion profile predicted from eq. (7) utilizing the rate constants calculated using eqs. (8)–(10), which have been taken from the literature.^{5–7}

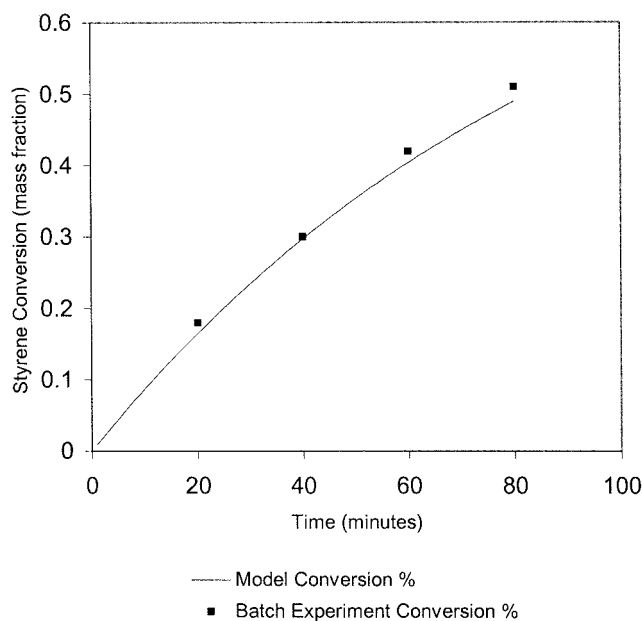


Figure 1 The batch and predicted time conversion behavior.

$$x = 1 - \exp\left\{-2k_p \sqrt{\frac{f[I]_0}{k_d k_t}} \left(1 - \exp\left\langle \frac{-k_d t}{2} \right\rangle\right)\right\} \quad (7)$$

where t is time (s), $[I]$ is the initiator concentration at $t = 0$ (mol/L), k_d is the kinetic rate constant of initiator dissociation (S^{-1}), k_p is the kinetic rate constant of propagation (L/mol s), k_t is the kinetic rate constant of termination (L/mol s), and f is the initiator effectiveness factor.

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

$$fk_d = 6.378 \times 10^{13} \exp\left(\frac{-29700}{RT}\right) \quad (8)$$

$$f = 0.8$$

$$k_p = 10^{7.630} \exp\left(\frac{-7740}{RT}\right) \quad (9)$$

$$k_t = 1.255 \times 10^9 \exp\left(\frac{-1675}{RT}\right) \quad (10)$$

where R is the universal gas constant (cal/mol K).

The experimental data and predicted conversions are in good agreement. These rate constants have been used in all subsequent calculations.

In the same work it was concluded that the conversion of a single pass of the SDR was a function of both the conversion of polymer feed and the rotation rate of the disk. This was attributed to the role of each in controlling the residence time of the fluid on the disk.

TABLE I
Kinetic Parameters to Achieve 10% Conversion in 5 s

Variable	Batch reactor (363 K)	Required for SDR conversion (363 K)	Factor
k_t	1.23E8	1.8E3	$7E4^{-1}$
k_p	9.27E2	2.3E5	250
k_d	8.18E-5	NA	NA

Thus, a higher conversion feed with high viscosity would reduce the rate of radial acceleration to increase the residence time. The results of all tests can be broadly simplified as each pass of the disk results in monomer conversions of around 10%.

Kinetic analysis of sdrs

Equation (7) is not directly applicable to the SDR because the time to a steady state for the styrene system is similar to the fluid residence time. However, the model has been used to gain some insight into the magnitudes of change of each kinetic parameter required to achieve conversions that are typical of a single pass over the disk. Typical SDR conditions are: a single pass over the disk will achieve a conversion from 30 to 40% with a residence time of 5 s. Initially a feed of 225 mL styrene, 45 mL toluene, and 3.375 g BPO is reacted in a batch reactor and then fed over the SDR.

Because of assumptions made in the derivation of the model, it is not possible to adjust the k_d value to predict the correct conversion. Higher values of k_d act to increase the equilibrium radical concentration. This acts to increase the propagation rate, which is first order in radical concentration, but also acts to greatly increase the rate of termination, which is second order in radical concentration. Thus, increasing the radical pool concentration via increasing the k_d acts to produce a low molecular weight polymer; eventually the polymerization ceases once the initiator is consumed. This dead stop can occur before the required conversion is achieved.

The remaining two parameters (k_p and k_t) can be adjusted so that a conversion of 10% can be predicted in 5 s (Table I). This was accomplished by either increasing k_p by a factor of 250 or reducing k_t by a factor of 70,000. Both of these cases are further discussed below.

Rates of polymerization with limited termination reactions

To investigate this scenario it is assumed that the conditions on the spinning disk minimize termination by combination or disproportionation reactions. It has been suggested that bimolecular reactions may be reduced in an SDR environment due to centrifugal

forces and the divergent nature of the flow acting to radially align the chains, preventing them from coming together. This phenomenon would result in a buildup in the propagating radical concentration (mol/L) from the equilibrium concentration calculated from eq. (11).

$$R_{eq} = \sqrt{\frac{fk_d[I]}{k_t}} \quad (11)$$

For this calculation it is assumed that terminations by bimolecular reactions are prevented on the disk, such that $R_t = 0$. In this case no equilibrium radical concentration will exist as the pool will continuously increase as more BPO decomposes. The rate of radical generation (R_{rg}) and polymerization (R_p) can be calculated using eqs. (12) and (13) (mol/L s).

$$R_{rg} = 2fk_d[I] \quad (12)$$

$$R_p = K_p[M][R^*] \quad (13)$$

Equations (12) and (13) have been linearized over 50-ms time steps and solved simultaneously to estimate the evolution of the radical population with time and the subsequent increase in the propagation rate. The radical buildup and change of styrene conversion with time can be seen in Figure 2. Note from Figure 2 that a conversion of 10% is achieved after approximately 5 s. This conversion is similar to typical SDR time conversion behavior.

Rates of polymerization with enhanced propagation kinetics

In the second scenario it is assumed that the conditions on the disk act to increase the value of k_p . This may arise because of the flow extension or centrifugal field acting to increase the reactivity of the radical on the propagating end of the chain. In this case the

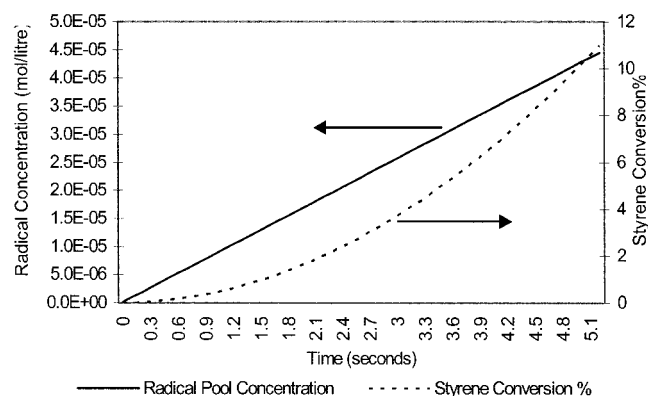


Figure 2 The buildup of radical concentration and styrene conversion as a function of time.

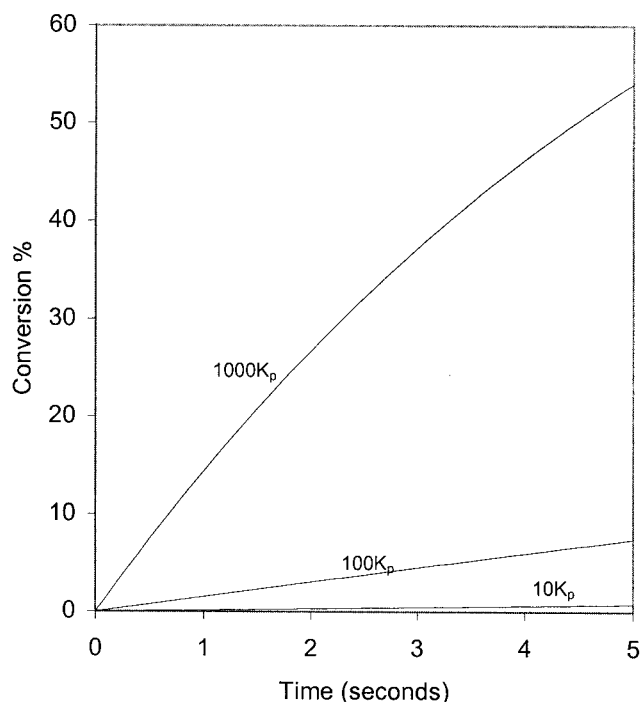


Figure 3 The effect of increasing the k_p on the evolution of conversion with time.

equilibrium radical concentration remains constant, the rate enhancement being directly caused by an increase in the propagation rate.

The sensitivity of the time conversion behavior has been investigated by predicting the overall conversion over a 5-s period. The effect of a 10-, 100-, and 1000-fold increase in the k_p can be seen in Figure 3. A conversion of approximately 10% is achieved in 5 s when k_p is increased by a factor of 100. Although this solution has been shown to be mathematically possible the remainder of this work will concentrate on the first scenario to assess if the ideas proposed in our earlier publication¹ can hold.

End group analysis

For both of the scenarios described above the number-average molecular weight (M_n) of the product can be calculated by equating the moles of BPO cleaved in one pass to the moles of styrene polymerized in that pass. Based on a 1-L system, it can be calculated that in the 5-s residence time on the disk, 4.264E-6 mol of BPO cleave to produce 8.528E-6 mol of BPO derived end groups (BPO_{eg}). For the purpose of this calculation it is assumed that $f = 1.0$ and no decarboxylation of the benzoyloxy radical occurs. During the same time, 10% styrene conversion occurs, equating to 0.718 mol of styrene (S_{conv}). If it is assumed that termination occurs via radical combination, then

$$M_n = M_{w\text{sty}} \frac{S_{\text{conv}}}{1/2 \times \text{BPO}_{\text{eg}}} \quad (14)$$

where $M_{w\text{sty}}$ is the molecular weight of styrene.

Solving eq. (14) yields an average molecular weight of 3.5E6 g/mol. The value of 0.5 in the numerator reflects the presence of a BPO derivative on both ends of the chain. If termination occurs via disproportionation, then a BPO derivative group only exists on one end; thus, the molecular weight can be calculated to be 1.75E6 g/mol.

During the SDR tests the M_n of the polymer produced on the disk was measured to be less than 30,000 g/mol. Therefore, it can be concluded that, if enhanced rates of polymerization are due to either an increase in k_p or reduction in k_t , then some other reactions become important in the control of the molecular weight. The following section discusses the possibility of chain transfer reactions being important on an SDR.

Chain transfer effects

Chain transfer can act to control molecular weight distributions in polymerization systems. In a chain transfer reaction an atom, usually hydrogen, is transferred from a component in the system to the growing polymer chain. This transfer prevents further growth of the polymer chain, but it does produce a radical that may propagate another chain. For the current system, transfer to styrene, toluene, and polymer have all been found to be appreciable. However, for batch systems at 60°C with 2 wt % BPO, transfer to the initiator has been found to be the dominant pathway of termination.⁶ In the current system 1% (w/w) BPO is used to initiate the reaction. In this work it is assumed that the transfer to initiator is the dominant transfer reaction, at least for the case with high initiator concentrations. The transfer to initiator constant for the BPO/styrene/toluene system has been measured to be 0.813 at 80°C.⁸ Here we assumed that the activation energy for both propagation and transfer reactions are similar, such that the constant will be similar at 90°C; therefore,

$$C_t = k_{tr}/k_p = 0.81 \quad (15)$$

at 90°C.

It is important to note that either an increase in k_p or a decrease in k_t maintains a fixed ratio between the propagation rate and transfer rate. In the case of increased k_p , this is due to the direct relationship of eq. (15). For the case of a reduced k_t , a radical population increase is predicted; as propagation and transfer reactions are both first order with respect to radical concentrations, both will increase at a similar rate. For

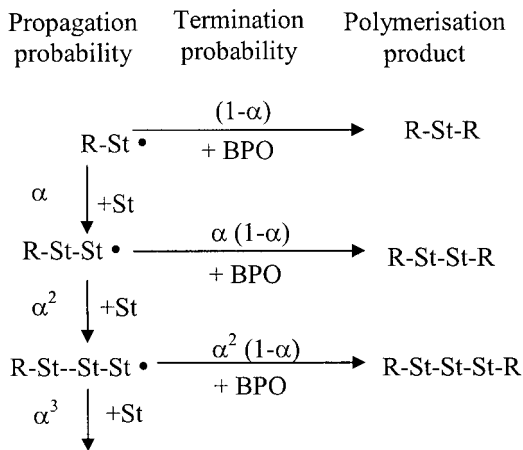


Figure 4 The probability of propagation versus transfer.

both systems it can be shown that transfer is rapid compared to termination by bimolecular reactions. Thus, at least to a first approximation, the molecular weight of the product is strongly controlled by the transfer reaction, such that the weight of this product can be calculated using the same technique.

A polymer chain grows by the sequential addition of monomer units. For each addition there is a probability that some other reaction will occur that results in termination of that chain. From this definition a chain growth probability factor can be defined as

$$\alpha = \frac{R_p}{R_p + R_{tr} + R_t} \quad (16)$$

For the current case it is assumed that $R_t = 0$. Substituting eq. (15) into (16) and simplifying,

$$\alpha = \frac{[M]}{[M] + (C_t[I])} = 0.994 \quad (17)$$

The chain growth probability expresses the probability that a chain will react with a monomer molecule as opposed to it reacting with a BPO molecule. The molar distribution for all products can be calculated using a Flory–Anderson–Schultz probability distribution (Fig. 4).

Once the molecular weight is calculated, it can be manipulated to form the mass distribution from which number-average (M_n) and weight-average (M_w) molecular weights are calculated. An example of such a distribution is shown in Figure 5.

It can be shown that the number and weight average can be calculated from the chain growth probability factor using eqs. (18) and (19).⁹ These equations provide a quick and easy method to calculate such averages.

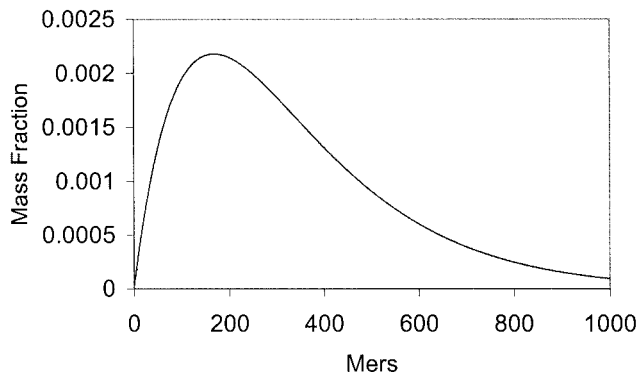


Figure 5 An example of a calculated weight distribution.

$$M_n = M_{wsty} \frac{1}{1 - \alpha} \quad (18)$$

$$M_w = M_{wsty} \frac{1 + \alpha}{1 - \alpha} \quad (19)$$

For the current system with $\alpha = 0.994$, the M_n is calculated to be around 18,000 g/mol.

Model validation

In order to validate the SDR reaction model a series of SDR runs were simulated. For the model validation it is assumed that the rate enhancement is due to the hydrodynamics on the disk preventing bimolecular termination reactions as proposed in an earlier publication.¹ In the SDR runs a batch reactor was used to react the mixture to a predetermined extent; the prepolymer mix was then fed onto the SDR and the conversion measured. The results of the test are summarized in Table II.

To simulate the SDR, the residence time on the disk and feed composition onto the disk must be calculated. The method used to calculate these parameters is now described. Emslie et al.¹⁰ have developed theoretical equations to describe the flow of a Newtonian fluid on a rotating disk. If it is assumed that the centrifugal force is balanced by the fluid's viscous drag, then it can be shown that the residence time on a SDR can be estimated using eq. (20) below.

TABLE II
Experimental Data

Test no.	Time in batch (min)	SDR feed conversion (%)	SDR product conversion (%)	Conversion achieved in pass (%)
1	60	42.0	47.8	5.8
2	80	52.0	61.5	9.5
3	90	56.0	65.4	9.4

TABLE III
Feed Conditions

Test no.	Time in batch (min)	Residence time (s)	Styrene concentration (mol/L)	BPO fraction remaining
1	60	4.52	4.16	0.75
2	80	7.99	3.47	0.67
3	90	8.43	3.15	0.64

$$t_r = \frac{3}{4} (12\pi^2)^{1/3} \left(v \frac{(r_e^4 - r_i^4)}{\omega^2 Q^2} \right)^{1/3} \quad (20)$$

where v is the kinematic viscosity (m^2/s), ω is the angular velocity (rad/s), Q is the flow rate (m^3/s), r_e is the radius of the disk (m), and r_i is the radial position of the feed (m).

To estimate the BPO concentration in the feed to the SDR, the rate of decomposition has been calculated using eq. (8). The feed conditions on the SDR are summarized in Table III. The residence time has been calculated from eq. (20) using viscosity data collected in a cone and plate viscometry study.¹¹ The three tests have been simulated by assuming that bimolecular termination does not occur on the disk. For this case the rate of reaction can be calculated using eqs. (12) and (13). Again, the reactions have been linearized over 50-ms time steps and the change in conversions calculated. The experimental and predicted conversions are shown in Figure 6.

It can be seen that the model qualitatively predicts the effect of the increased viscosity and reduced monomer and initiator concentrations. It is interesting

to compare the results between tests 2 and 3. Even though the residence time is increased for test 3, a lower conversion is predicted by the model. This is due to the depletion of both monomer and initiator having a stronger effect on the overall rate of polymerization than the increase in residence time. This counterintuitive effect was also measured experimentally.

For all tests the model underpredicts the conversion of a single pass by approximately 2%. The reason for this underestimation is not yet known. It is possible that it is attributable to an error in the calculation of the residence time or errors in the kinetic data. It is also possible that the reaction proceeds on the wall of the SDR until the mixture is quenched and the radical pool falls to typical batch concentrations. It is difficult to comment further on the shortfall; however, these points are being further investigated.

DISCUSSION

It has been shown that conversions typical of an SDR can be estimated by combining a centrifugal model to estimate disk residence times with the assumption that k_d is reduced to zero. Physically this would represent mechanical prevention of two propagating polymer chains terminating through bimolecular reactions. For this case the molecular weight of the product is controlled by transfer reactions. Using the models developed the effect of the initiator concentration on conversion in 5 s and the molecular weight of the product have been investigated. It was mathematically found that typical rate enhancements can be

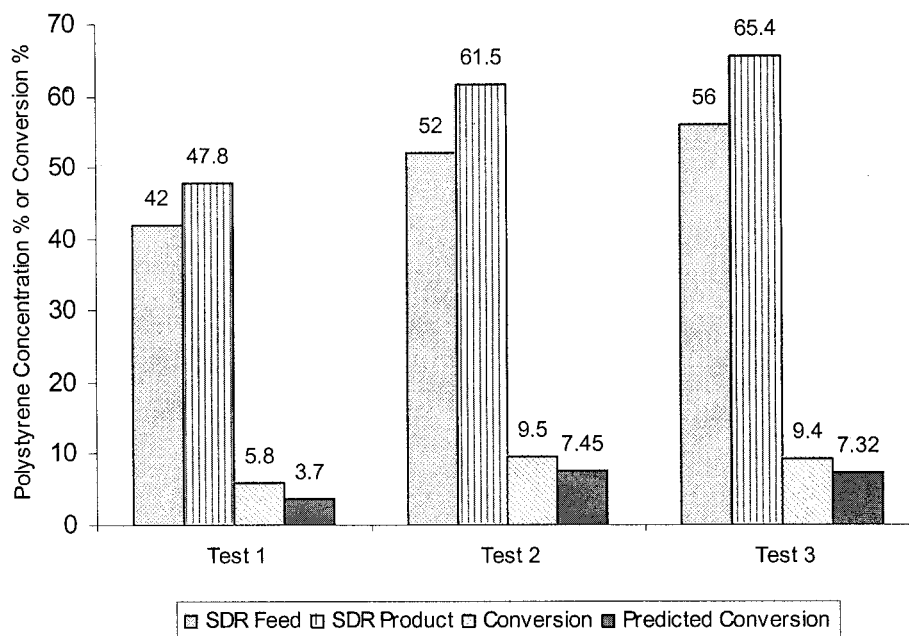


Figure 6 A comparison of the experimental and predicted conversions.

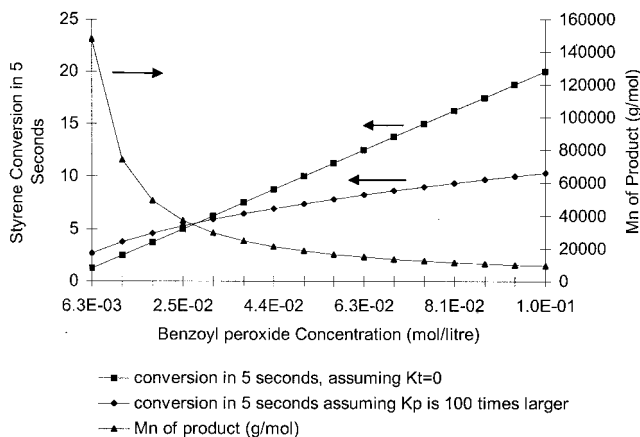


Figure 7 Conversion and product molecular weight predictions as a function of the BPO concentration at 90°C.

explained by either an increase in k_p by a factor of 100 or in the case of reduced bimolecular termination, $k_t = 0$. For the current system, the predicted effect of the initiator concentration can be seen in Figure 7.

It is interesting to note the different shapes of the predicted increase of conversion with increasing initiator concentration. The scenarios of the reduction of k_t having linear behavior and increasing k_p have a root dependence on the initiator concentration. It is hoped that the experimental results will provide evidence to comment further on this topic.

A second implication of the model is that for the current system high conversions per pass while producing a high molecular weight product is not possible using an SDR. However, it has been shown that transfer to the initiator is very likely to be important in controlling the product spectrum. Therefore, if an initiator with a low transfer constant is utilized, both high conversions per pass and high molecular weight products should be achievable. The experimental study parallel with the numerical study will investigate if this is achievable. It is

thought that as the transfer to initiator becomes slower, secondary transfer reactions such as transfer to monomer, solvent, or polymer will begin to control the product spectrum. However, the transfer constants for these reactions are low and so a high molecular weight product will be possible.

CONCLUSION

This work was carried out in an attempt to gain insight into the changes that must occur in the mechanisms operating in a conventional free-radical polymerization in order to achieve the observed rates when using an SDR. It was shown that, if the conventional system operates with an increased k_p or reduced k_t , rates can be sufficiently enhanced to explain the dramatic rate increase. Further experimental work is due to commence, so it is hoped that the findings of the work will forward our understanding of the mechanism of this unique phenomena.

References

1. Boodhoo, K. V. K.; Dunk, W. A. E.; Jachuck, R. J. *J Appl Polym Sci* 2002, 85, 2283.
2. Boodhoo, K. V. K.; Jachuck, R. J. *Green Chemistry* 2000, 2, 235.
3. Matyjaszewski, K.; Davis, T. P. *Handbook of Radical Polymerization*; Wiley: New York, 2002; Chapters 3 and 4.
4. Boodhoo, K. V. K.; Jachuck, R. J. *Appl Therm Eng* 2000, 20, 1127.
5. Biesenberger, J. A.; Sebastian, D. H. *Principles of Polymerization Engineering*; Wiley: New York, 1983; Chapter 1.
6. Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerisation*; Elsevier: Oxford, U.K., 1995; Chapter 3.
7. Buback, M.; et al. *Macromol Chem Phys* 1995, 196, 3267.
8. Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989.
9. Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991; Chapter 3.
10. Emslie, A. G.; Bonner, F. T.; Peck, L. G. *J Appl Phys* 1958, 29, 858.
11. Boodhoo, K. Ph.D. Thesis, University of Newcastle, Newcastle, U.K.; 1999.