

The Influence of Reactor Type and Operating Conditions on the Molecular Weight Distribution in Vinyl Acetate Polymerization

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Synopsis

The vinyl acetate polymerization system was investigated with respect to the breadth of the molecular weight distribution (MWD) in batch, continuous segregated, and continuous micromixed reactors. Models were developed employing a complex kinetic scheme including polymer transfer and terminal double bond polymerization, without neglecting initiation and termination steps. Inclusion of a gel effect for terminal double bond polymerization gave better agreement with experimental molecular weight data in suspension polymerization. Simulation results showed the MWD order in the three reactor types is not fixed, but a function of reactant concentrations and the importance of chain branching. In some cases changing the initiator type and concentration will change the MWD order.

INTRODUCTION

Several authors have studied the vinyl acetate polymerization system to determine the effects of micro- and macromixing and reactor type on the MWD.¹⁻¹⁰ Different research groups have presented apparently contradictory results with respect to the degree of MWD broadening observed in batch (BR), homogeneous micromixed continuous stirred reactors (HCSTR), and completely segregated continuous stirred reactors (SCSTR). Baade et al.¹ and Baade² experimentally found that the HCSTR produced the narrowest MWD, while the broadest MWD was observed in the SCSTR, and the BR produced polymer with a MWD lying in between. Graessley et al.³⁻⁷ and Villiermaux et al.⁸⁻¹⁰ determined a different order with respect to the MWD in the three reactor types, showing the broadest MWD in the HCSTR, the narrowest MWD in the BR, with the SCSTR lying in between. Tadmore and Biesenberger¹¹ demonstrated that, in free radical polymerization without chain branching, the broadest distribution should be obtained in the SCSTR and the narrowest in the HCSTR.

The vinyl acetate polymerization system exhibits chain branching which exerts a strong influence on the MWD of polymer produced. Branch points are introduced in polymer molecules by reaction of growing radicals with chains formed earlier in the polymerization, and by terminal double bond polymerization (TDBP). These branching reactions are highly sensitive to residence time distribution and mixing effects, and broaden the MWD.

In the BR, all polymer molecules will have the same length of reaction time, but monomer and initiator concentrations will change with time, broadening the MWD. In the HCSTR, where perfect mixing is achieved on

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the molecular level, reaction products will have a distribution of times in the reactor, but monomer and initiator concentrations will be constant. Denbeigh¹² mentioned that for free radical polymerization, where the radical chain lifetime is significantly less than typical reactor residence time values, the HCSTR will give product unaffected by the residence time distribution. In the SCSTR, where the reaction mass consists of small batch reactors with no mixing on the molecular level, polymer molecules will react in an environment with changing monomer and initiator concentrations. In this case the product will consist of molecules produced from a set of batch reactors where the reaction has proceeded for different times. When chain branching is present, this will tend to broaden the MWD in the HCSTR more than in the BR or SCSTR, because the average polymer concentration is always at a higher level at a given conversion. The relative importance of MWD broadening factors present in the three reactor types will determine the MWD order.

SPECIFICATION OF THE KINETIC SCHEME

A kinetic scheme for vinyl acetate polymerization was employed in which species both with and without a terminal double bond were considered. Termination is assumed to be by disproportionation, because this is the main mode of termination in vinyl acetate polymerization.^{1,8-10,13-15} It was also assumed that each polymer chain has no more than one radical or one terminal double bond.

Initiation:



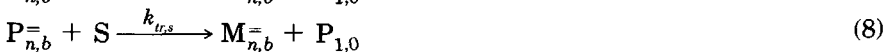
Propagation:



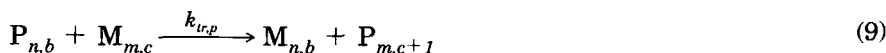
Chain transfer to monomer:

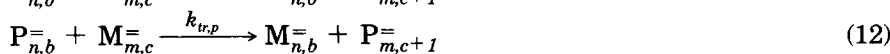
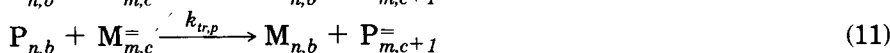
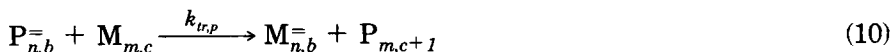


Chain transfer to solvent:



Chain transfer to polymer:

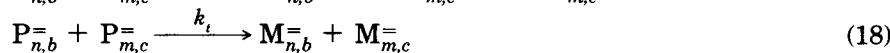
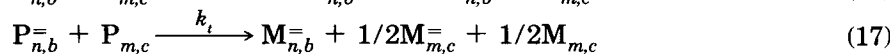
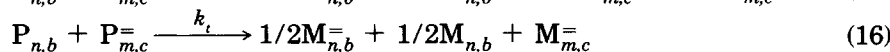




Terminal double bond polymerization:



Termination by disproportionation:



Here I is initiator, R⁻ is an initiator fragment, P_{n,b} and M_{n,b} are live polymer radicals and dead polymer molecules with *n* monomer units and *b* branches, P_{n,b}⁻ and M_{n,b}⁻ are live polymer radicals and dead polymer molecules with *n* monomer units, *b* branches, and a terminal double bond, M is monomer, and S is solvent.

MODEL FORMULATION

Mathematical models were formulated for BR, HCSTR, and SCSTR cases. The basic relations consist of monomer, initiator, moment, and gel effect equations. The batch case is discussed here, since the relations for the other reactor types follow from these. Volume effects were assumed to be negligible, as shown by Baade et al.¹ for monomer conversion.

The BR relations for monomer and initiator conversion are given by

$$\frac{dX_m}{dt} = -\frac{1}{M_0} \frac{dM}{dt} = k_p(1 - X_m)\lambda_{0t} \quad (19)$$

and

$$\frac{dX_I}{dt} = -\frac{1}{I_0} \frac{dI}{dt} = k_d(1 - X_I) \quad (20)$$

where λ_{0t} is the total concentration of free radicals:

$$\lambda_{0t} = \left(\frac{2fk_dI}{k_t} \right)^{1/2} \quad (21)$$

which is also the zeroth live moment of the MWD. In this analysis the

initiation and termination reactions were considered to be important, as illustrated in the kinetic model. Graessley et al.³⁻⁷ and Hamielec¹³ have modeled this system neglecting initiation and termination steps, although at higher initiator concentrations these are not necessarily negligible. Hyun et al.¹⁵ later extended the models to include initiation and termination reactions. Hamer,¹⁶ Villermaux et al.⁸⁻¹⁰ and Taylor and Reichert¹⁷ also simulated this system including initiation and termination steps in the MWD equations.

To determine the behavior of the MWD, the method of moments was used as described by Ray.¹⁸ The polymer radical moments are defined by

$$\lambda_i^- = \sum_{r=1}^{\infty} \sum_{b=0}^{\infty} r^i P_{r,b}^- \quad (22)$$

$$\lambda_i = \sum_{r=1}^{\infty} \sum_{b=0}^{\infty} r^i P_{r,b} \quad (23)$$

where the $-$ indicates a terminal double bond is present in the system, and two separate populations are considered, both with and without terminal double bonds. The polymer molecule moments are given by

$$\nu_i^- = \sum_{r=1}^{\infty} \sum_{b=0}^{\infty} r^i M_{r,b}^- \quad (24)$$

$$\nu_i = \sum_{r=1}^{\infty} \sum_{b=0}^{\infty} r^i M_{r,b} \quad (25)$$

The number and weight average molecular weights are determined from

$$M_n = M_{va} \left(\frac{\lambda_{1t} + \nu_{1t}}{\lambda_{0t} + \nu_{0t}} \right) \quad (26)$$

$$M_w = M_{va} \left(\frac{\lambda_{2t} + \nu_{2t}}{\lambda_{1t} + \nu_{1t}} \right) \quad (27)$$

where M_{va} is the molecular weight of vinyl acetate, and

$$\lambda_{it} = \lambda_i^- + \lambda_i \quad (28)$$

$$\nu_{it} = \nu_i^- + \nu_i \quad (29)$$

The polymer radicals are considered in M_n and M_w , since in some cases these can make a significant contribution^{13,19} to the MWD. The polydispersity Q is given by

$$Q = M_w / M_n \quad (30)$$

By writing mass balances for the species $P_{r,b}$, $P_{r,b}^-$, $M_{r,b}$, and $M_{r,b}^-$ and performing the summations given, Eqs. (22)–(25) allow moment relations to be obtained for polymer radicals and polymer molecules. The quasi-steady-state assumption was applied to the radical species, an assumption shown to be valid by Hamielec et al.²⁰ and Ray²¹. After some manipulation, the following relations are obtained, in a manner similar to Hamer¹⁶:

$$\lambda_{i^-} = \alpha \left\{ k_p M \left[\sum_{k=0}^i \binom{i}{k} \lambda_k^- - \lambda_i^- \right] + k_{tr,m} M \lambda_{0t} + k_{tr,p} \lambda_{0t} \nu_{i+1}^- + k_{pdb} \left[\sum_{k=0}^i \binom{i}{k} \lambda_k^- \nu_{i-k}^- - \nu_0^- \lambda_i^- \right] \right\} \quad (31)$$

$$\lambda_i = \alpha \left\{ k_p M \left[\sum_{k=0}^i \binom{i}{k} \lambda_k - \lambda_i \right] + k_{tr,s} S \lambda_{0t} + k_t \lambda_{0t}^2 + k_{pdb} \left[\sum_{k=0}^i \binom{i}{k} \lambda_k \nu_{i-k}^- - \nu_0^- \lambda_i \right] + k_{tr,p} \lambda_{0t} \nu_{i+1} \right\} \quad (32)$$

where

$$\alpha = \frac{1}{k_{tr,m} M + k_{tr,s} S + k_{tr,p} \nu_{1t} + k_t \lambda_{0t}} \quad (33)$$

and

$$\frac{d\nu_{i^-}}{dt} = k_p M \left[\sum_{k=0}^i \binom{i}{k} \lambda_k^- - \lambda_i^- \right] + k_{tr,m} M \lambda_{0t} + k_{pdb} \left[\sum_{k=0}^i \binom{i}{k} \lambda_k^- \nu_{i-k}^- - \nu_i^- \lambda_{0t} - \nu_0^- \lambda_i^- \right] + \frac{k_t}{2} \lambda_i \lambda_{0t} \quad (34)$$

$$\frac{d\nu_i}{dt} = k_p M \left[\sum_{k=0}^i \binom{i}{k} \lambda_k - \lambda_i \right] + k_{tr,s} S \lambda_{0t} + k_t \lambda_{0t}^2 + k_{pdb} \left[\sum_{k=0}^i \binom{i}{k} \lambda_k \nu_{i-k}^- - \nu_0^- \lambda_i \right] - \frac{k_t}{2} \lambda_i \lambda_{0t} \quad (35)$$

Upon examination of Eqs. (31) and (32), one notices that reference to $(i + 1)$ th polymer molecule moments is made. To obtain closure of this system of equations, it was assumed that the highest order (n th) polymer molecule moment distribution is divided into fractions with and without terminal double bonds in the same proportion as the $(n - 1)$ th moment is found to be distributed, and only the total molecule moment relation is considered in the n th case. This gives the relations

$$\nu_n^- = \nu_{nt} (\nu_{n-1}^- / \nu_{n-1,t}) \quad (36)$$

$$\nu_n = \nu_{nt} (\nu_{n-1} / \nu_{n-1,t}) \quad (37)$$

This approximation was tested by considering the cases, where 2, 3, 4, and 5 orders of moment equations were written, and this was also compared to results from using the method of Villermaux et al.⁸⁻¹⁰

Solutions for HCSTR and SCSTR reactors are found from the batch case relations with some modifications. For a property P_i in the batch case,

$$\frac{dP_{i,BR}}{dt} = F_i(\mathbf{P}, t) \quad (38)$$

For the HCSTR,

$$P_{i,HCSTR} = \tau F_i(\mathbf{P}, \tau) + P_{i,0} \quad (39)$$

where τ is the reactor residence time. For the SCSTR,

$$P_{i,SCSTR} = \int_0^\infty P_{i,BR} E(\theta) d\theta \quad (40)$$

where²²

$$E(\theta) = \exp(-\theta) \quad (41)$$

with

$$\theta = t/\tau \quad (42)$$

The SCSTR case was also simulated with a more general expression for n -SCSTRs in series where a different expression for the residence time distribution in eq. (41) is used, as discussed by Taylor and Reichert.¹⁷

REACTOR SIMULATION

Programs were written for the BR, HCSTR, and SCSTR cases. Temperature effects were included, and the relations were solved in terms of dimensionless variables. Provisions were made for including gel effects in termination, propagation, and TDBP. The BR relations were solved by integrating monomer and initiator conversion relations and moment equations using the Gear method.²³ The batch system was also simulated with conversion as the dependent variable.

The SCSTR was simulated by integrating the BR solutions with the residence time distribution expression as illustrated in eq. (41) using either a Simpson's rule integration scheme or Laguerre polynomials.²⁴

For the HCSTR, the equations from the batch case were modified to include species inflow and outflow terms and the time-dependent HCSTR relations were integrated for 10 residence times. Since in some cases steady state was not reached after 10 residence times, a Newton-Ralphson nonlinear equation solver was written,²⁵ and the steady state relations were solved with initial conditions determined from the time-dependent integration.

PARAMETER VALUES

One of the most important aspects of any investigation involving mathematical modelling is a proper consideration of the constants used. As illustrated in Table I, a wide range of kinetic parameters have been reported in the literature for the vinyl acetate polymerization (all at 60°C).

In this analysis, it was desired to first simulate the experimental results of Baade et al.¹ for the MWD values in the three reactor types, and to compare this with the trends of Graessley et al.³⁻⁷ Since Baade et al. used two reaction systems, suspension and solution, and since eight constants are necessary for MWD values in each system (not counting gel effect values), 16 constants could hypothetically be fitted. It was decided to use kinetic constants presented in the literature, and use one set of kinetic parameters for chain transfer to monomer, solvent, and TDBP. Graessley et al.^{3-7,15} has performed some of the most extensive studies on the vinyl acetate polymerization system, so that their kinetic constants for chain transfer and TDBP were selected, as shown in Table IIA. In the BR and SCSTR polymerization cases, which were performed in suspension, the propagation rate constant k_p was determined to best fit the BR conversion time data using the method of Marquardt.²⁸ All other constants listed here are from the literature.

A gel effect for the bulk vinyl acetate polymerization was determined by Reichert and Moritz²⁹ and Moritz.³⁰ Vinyl acetate was polymerized in bulk in a double slit rotational viscometer and the increase in viscosity was measured as a function of time. Moritz determined a correlation of the form:

$$\frac{k_p^2 f k_d}{k_t} \sim \exp(At) \quad (43)$$

And since individual values for propagation and termination constants are required, a gel effect was implemented as

$$G_t = k_t / k_{t0} = \exp(-At) \quad (44)$$

where A was determined from Moritz as

$$A = 5.81 \times 10^{-3} I_0^2 \quad (45)$$

Chatterjee et al.³ determined values of $C_{tr,p}$, the amount of chain transfer from polymer, and found that it is a strong function of the solvent concentration in solution polymerization. It was suggested the apparent reduction in $C_{tr,p}$ with dilution might reflect changes in the shielding of interior chain segments from free radical attack. Chatterjee et al.'s data were fitted to the relation

$$C_{tr,p} = 2.25 \times 10^{-4} \exp(-0.223\phi_s) \quad (46)$$

where ϕ_s is the solvent fraction relative to monomer, S/M_0 . From this

TABLE I
Parameters for Vinyl Acetate Polymerization Reported by Various Researchers—All at 60°C

Reference	<i>Polymer Handbook</i> ²⁶	Lindemann ¹⁴	Lindemann ²⁷	Chatterjee et al. ⁴	Chatterjee et al. ⁵
k_p (L mol ⁻¹ s ⁻¹)	7730– 19,000	3700	2505	—	—
k_t (L mol ⁻¹ s ⁻¹) × 10 ⁻⁸	3.8–7.6	0.740	0.304	—	—
k_d (s ⁻¹)	—	—	—	9 × 10 ⁻⁶	—
f	—	—	—	—	—
$C_{tr,m}$ × 10 ⁴	1.75–2.8	1.9–2.8	—	2.46	2.43
$C_{tr,s}$ × 10 ⁴	0.46–1.3	0.46–1.3	1.3	0.34	0.48
$C_{tr,p}$ × 10 ⁴	1.2–47.0	1.4–7.0	1.5	1.3	2.36
C_{pds}	—	0.80	0.80	0.66	0.66
$k_p/(k_t)^{0.5}$ (L mol ⁻¹ s ⁻¹) ^{0.5}	—	0.430	0.455	—	—
	Moritz ²⁰	Baade et al. ¹	Hamer ¹⁶	Villiermaux et al. ⁸	
k_p (L mol ⁻¹ s ⁻¹)	8000	9500	5150	11900	
K_t (L mol ⁻¹ s ⁻¹) × 10 ⁻⁸	7.0	3.55	3.93	0.728	
k_d (s ⁻¹)	2.2 × 10 ⁻⁴ + 4 × 10 ⁻³ I_0	—	9.36 × 10 ⁻⁶	9.25 × 10 ⁻⁶	
f	0.5	—	0.5	0.114	
$C_{tr,m}$ × 10 ⁴	—	2.38	2.39	2.15	
$C_{tr,s}$ × 10 ⁴	—	—	—	0.364	
$C_{tr,p}$ × 10 ⁴	—	3.4	1.18	3.03	
C_{pds}	—	0.66	0.66	0.226	
$k_p/(k_t)^{0.5}$ (L mol ⁻¹ s ⁻¹) ^{0.5}	0.302	0.504	0.260	1.39 (0.67) ^b	

^a Solvent tertiary butanol.

^b Adjusted for f being 0.5.

TABLE IIA
Kinetic Constants Used in the Vinyl Acetate Polymerization Simulations—All at 60°C

Parameter	Value	Reference
k_p (L mol ⁻¹ s ⁻¹)	9500 solution 3971 suspension	Baade et al. ¹ Optimal value
k_t (L mol ⁻¹ s ⁻¹)	3.55×10^8	Baade et al. ¹
k_d (s ⁻¹)	2.2×10^{-4} $+ 4. \times 10^{-3} I_0$	Moritz ³⁰
f	0.5	Moritz ³⁰
$C_{tr,m} \times 10^4$	2.46	Chatterjee et al. ⁴
$C_{tr,s}^a \times 10^4$	0.34	Chatterjee et al. ⁴
$C_{tr,p} \times 10^4$	0.520 solution 2.36 suspension	Chatterjee et al. ³ Chatterjee et al. ^{1,3}
C_{pdb}	0.66	Chatterjee et al. ⁴

TABLE IIB
Reactant Concentrations Used in the Vinyl Acetate Polymerization Simulations

System	M_0 (mol/L)	S (mol/L)	I_0 (mol/L)
Bulk or suspension	10.82	0	1.627×10^{-2}
Solution	1.407	9.26	2.115×10^{-3}

^a Solvent tertiary butanol.

relation a value of $C_{tr,p}$ for solution polymerization runs of Baade et al.¹ was obtained.

One final gel effect was implemented in a form analogous to that for termination, a TDBP gel effect. Since TDBP requires two polymer molecules to occur, it is logical that in bulk or suspension polymerization, as the conversion increases, the contribution from TDBP should decrease. A gel effect of the form:

$$G_{pdb} = k_{pdb}/k_{pdb0} = \exp(-Bt) \quad (47)$$

was implemented, where $B = 6.6 \times 10^{-4} \text{ s}^{-1}$, and better agreement with the data was obtained.

The monomer, solvent, and initiator concentrations used by Baade et al. are given in Table IIB. The initiator concentration was 0.5 wt % related to the monomer. For the polymerization in solution, 15 wt % monomer was dissolved in tertiary butanol. Dicyclohexyl peroxidicarbonate was used as the initiator, with a considerably higher initiator rate than that used in previous studies. Unless otherwise stated, all results presented are from the kinetic parameters and concentrations given in Table II.

RESULTS AND DISCUSSION

Model Comparison

Different methods were compared in the solution of the moment equations in batch vinyl acetate polymerization, as shown in Table III. Since the first

TABLE III
Comparison of BR Results Obtained from Different Moment Approximation Orders to Obtain Molecular Weights

Moment order n	X_m (%)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	Q
2	98.5	1.27	6.91	5.44
3	98.5	1.27	6.87	5.41
4	98.5	1.27	6.81	5.37
5	98.5	1.27	7.11	5.61
Villermaux method	98.5	1.40	7.02	5.02

three moments are needed to compute the molecular weights, it is logical to choose a higher-order moment relation to approximate the distribution of moments with and without terminal double bonds, and therefore three was chosen as the moment order for the results presented in this paper. Comparison of the results in Table III shows that the M_n values computed for $n = 2-5$ are the same, while the M_w values differ, with the largest deviation being between the fourth and fifth orders with a 4.3% difference between M_n and Q values.

Villermaux et al.⁸⁻¹⁰ has presented a method of modeling the system where only one species of each moment is considered (instead of balances with and without terminal double bonds), and a separate relation is used to determine the concentration of terminal double bonds. Villermaux used a mixing theorem to decouple the moment equations. Villermaux's method predicts M_n values higher (10.3% at 98.5% conversion in Table III and Q values lower (6.47%, $n = 3$). But the observed differences are of the order of experimental molecular weight measurement errors, and the trends observed are the same.¹⁷ In the absence of TDBP all five cases presented in Table III predict the same molecular weight values to three significant figures, as they should since in this case no approximations are involved in either solution method.

Baade et al.¹ determined that volume change effects in the vinyl acetate system have a negligible effect on conversion. Nevertheless, volume change effects were checked for the MWD, and a representative case showed the Q predicted at 98.6% conversion was 3.67% less in the bulk polymerization case, which again should have a negligible effect on the trends observed.

Experimental Data Agreement

Figures 1-3 illustrate comparisons of the models with experimental findings of Baade et al.¹ Figure 1 shows conversion as a function of time for the three reactor types. The BR and HCSTR results are obtained from suspension polymerization, and HCSTR results from solution polymerization, with the concentrations given in Table II. The HCSTR results are obtained from the kinetic parameters for yield of Baade et al. while the propagation constant k_p in the batch case was determined from an optimal fit.²⁸ The SCSTR yield simulations used the same constants as the BR, and as Figure 1 shows the data fits well, implying that it is truly an SCSTR.

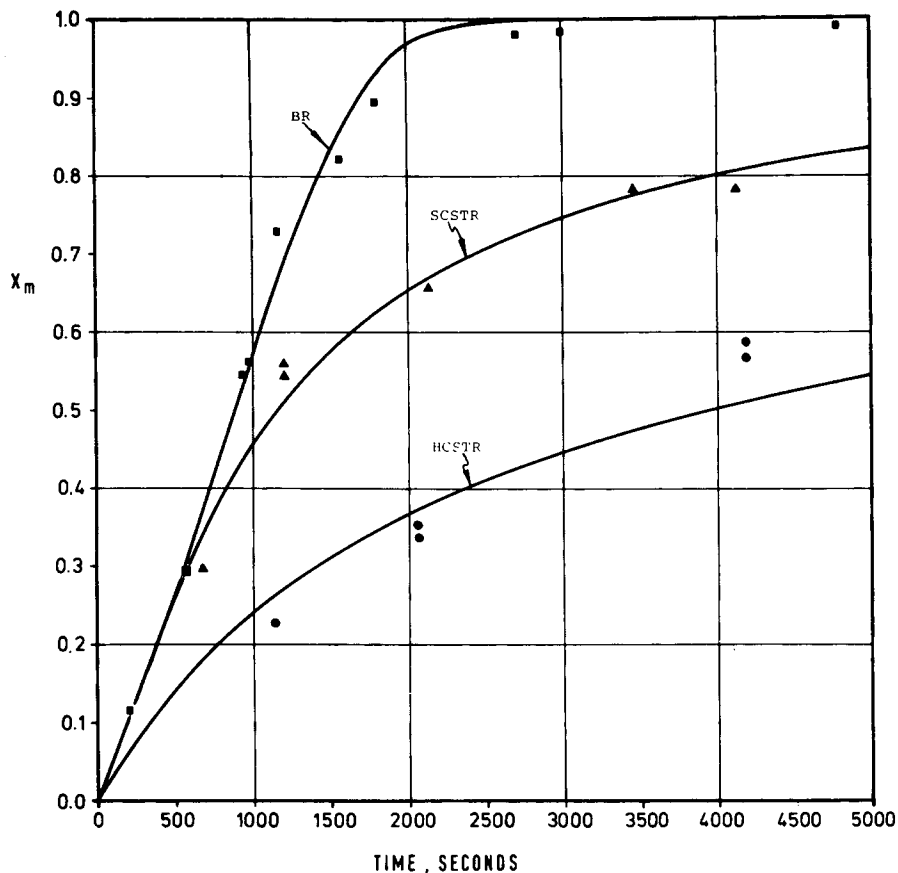


Fig. 1. Conversion as a function of time for the three reactor types compared with data of Baade et al.¹ BR and SCSTR results are from suspension polymerization, and HCSTR results from solution polymerization (kinetic parameters and concentrations from Tables IIA and IIB). (■) BR, (▲) SCSTR, (●) CSTR.

The polydispersity Q as a function of conversion is compared with the experimental results of Baade et al. in Figure 2. In this case all transfer and TDBP constants are taken from Chatterjee et al.³ In the BR and SCSTR cases, a gel effect for TDBP was included, as given in eq. (46). The constant B was found from an optimal least squares fit of the BR molecular weight data. Using the parameters of Graessley, the MWD broadening predicted from branching was too strong at high conversions, and in an earlier analysis¹⁷ the TDBP constant C_{pdb} was fitted to the BR data as demonstrated by the dashed lines in Figure 2. Including a TDBP gel effect and optimally fitting B instead of C_{pdb} allowed a better fit of the data, and the sum of squares error was reduced by approximately 40%. Comparison of the SCSTR cases with and without a TDBP gel effect shows the data agrees much better with the gel effect included. A wide range of parameter values were implemented between $C_{tr,p}$ and C_{pdb} and with a larger value of $C_{tr,p}$ the reactor simulations fit the data better, especially at lower conversions, but in all cases including the gel effect resulted in a better fit.

The ratio of the gel effect constants for termination and TDBP, A and

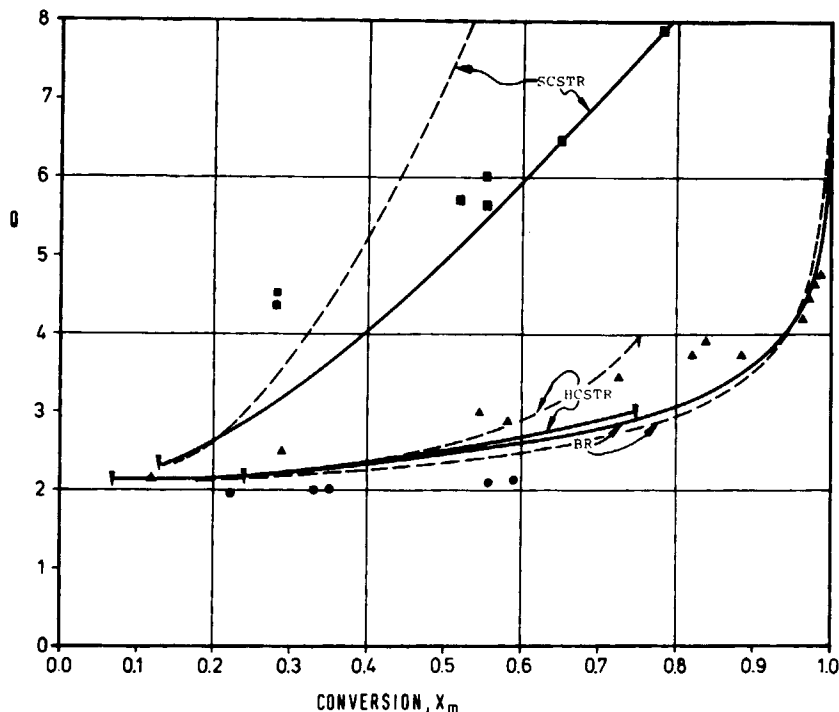


Fig. 2. Polydispersity Q as a function of conversion computed compared with the results of Baade et al.¹ BR and SCSTR results from suspension polymerization, and HCSTR results from solution polymerization (kinetic parameters and concentrations from Tables IIA and IIB). (—) Predictions with no terminal double bond polymerization gel effect; all reactors with the same values of polymer chain transfer, $C_{pdb} = 0.27$, $C_{tr,p} = 2.36 \times 10^{-4}$. (\blacktriangle) BR, (\blacksquare) SCSTR, (\bullet) HCSTR, (---) with and (—) without TDB gel effect.

B , should be approximately equal if chain entanglement is acting in the same way to reduce each mechanism, and for the system of Baade et al., the ratio is 3.9, quite close considering uncertainties in the other parameters. A gel effect for propagation (or glass effect) was tested at higher conversions, where k_p decreases as the reaction proceeds. In this case Q was greater at a given conversion with the gel effect, indicating that if this is included then the TDBP gel effect should be stronger. From the limited data presented here and the overall uncertainties in kinetic constants, the existence of a TDBP gel effect is definitely not proved, but these simulation results point the way for future investigations.

In Figure 2 the predictions of the HCSTR indicate the Q_{HCSTR} lies above Q_{BR} , contrary to that determined by Baade et al.¹ In the solid line case, Q_{HCSTR} is slightly above Q_{BR} , while the dotted line case has Q_{HCSTR} considerably above Q_{BR} . The dotted line case was computed using the same constant for polymer transfer in both suspension and solution polymerization cases, as done by Taylor and Reichert.¹⁷ Chatterjee et al.³ found a strong solvent effect on polymer transfer, and observed that, as the solvent concentration increased, the polymer chain transfer decreased as discussed earlier. In the experiments of Chatterjee et al., polymer chain transfer

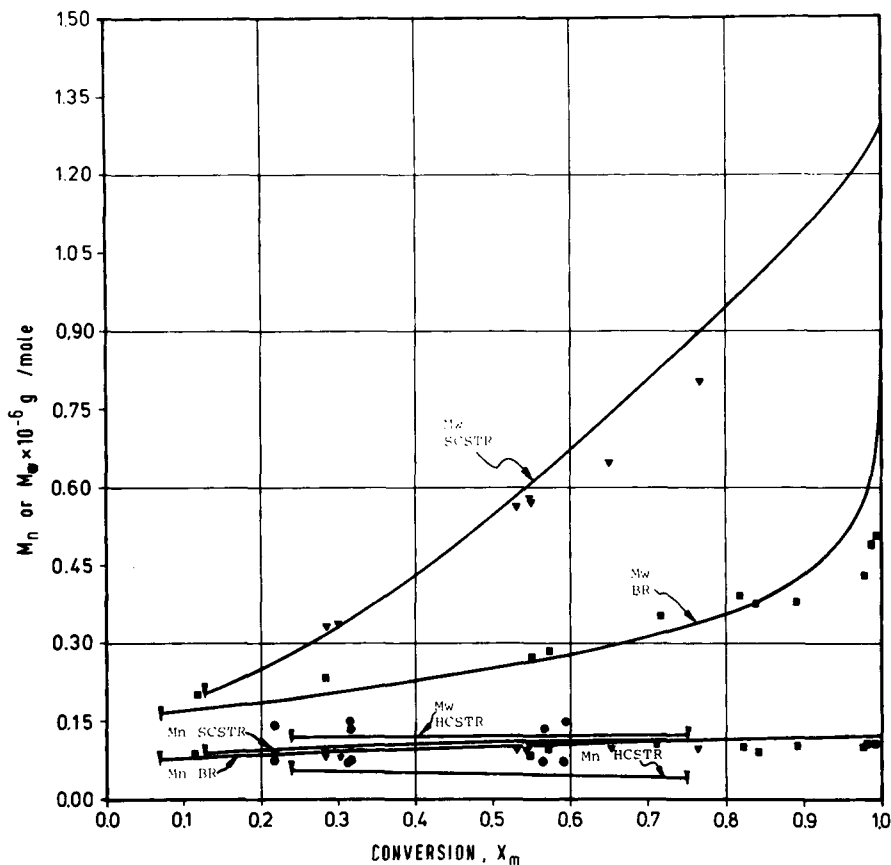


Fig. 3. M_n and M_w calculated from the experimental conditions of Baade et al.¹ BR and SCSTR results from suspension polymerization, and HCSTR results from solution polymerization (kinetic parameters and concentrations are given in Tables IIA and IIB). (■) BR, (▼) SCSTR, (●) HCSTR.

should be approximately five times less in the solution polymerization studies than in the suspension cases according to Graessley.

For a wide range of simulation parameters investigated, Q_{HCSTR} was never exactly 2, but always greater. Perhaps in the HCSTR runs another molecular weight modifying mechanism was present, such as inhibition, which was not included in the model, and this could change the results. Examination of the data from Baade et al. shows that the side chain branching of the HCSTR was greater than that of the BR, determined by removal of the hydrolyzable side chains and comparing the changes in molecular weight values. This implies that some MWD broadening from branching must be present. In the data analysis of Baade et al. the absolute values of M_n were determined by membrane osmosis, while gel permeation chromatography with a differential refractometer detector was used to obtain M_w values. Since the HCSTR experiments were in solution, and the monomer concentration was 1.407 mol/L vs. 10.82 mol/L in the suspension polymerization cases, the HCSTR M_n values were approximately 25% low-

er than the BR and SCSTR cases. This could have caused problems with M_w determinations in the HCSTR.³¹

The molecular weight values are compared in Figure 3 from the data of Baade et al. The BR and SCSTR values show good agreement between experimental data and theoretical predictions especially considering that no undue parameter fitting has been done. In the HCSTR case, the data lies above that of the model predictions.

Chatterjee et al.⁴ performed experiments in a continuous stirred tank reactor (CSTR) to match the HCSTR model predictions from his models, and found that the experimentally measured M_w values were below those predicted from both HCSTR and SCSTR models, although the data were close to the predictions for an SCSTR. Three main explanations were investigated; first, as pointed out by Jackson et al.,¹⁹ radical outflow terms were neglected in Chatterjee et al.'s analysis, although calculations showed this effect should be important only at higher polydispersity values ($Q > 10$). The second explanation given was the time required for M_w to reach steady state values, and the third hypothesis was segregation present in the CSTR. The second hypothesis for the HCSTR was investigated here by suppressing the Newton-Ralphson nonlinear equation solver in the HCSTR program and solving monomer, initiator, and moment relations with time dependence. Chatterjee et al. found that the HCSTR could take more than 10 residence times for M_w values to reach steady state and observed that M_w rose steadily to a steady state value. Simulations using their reactant concentrations showed that in six residence times, M_w was 94% of M_w at steady state (60% conversion) and at 10 residence times steady state was effectively reached, agreeing with their findings. Chatterjee et al. also simulated the SCSTR with initial effects included, and found that after essentially three residence times a steady state M_w was obtained. Their experiments measured conversion and molecular weight transient effects by measuring refractive index and stirrer torque (solution viscosity), and after two residence times steady readings were found, more consistent with the SCSTR case.

The HCSTR runs of Baade et al.¹ were also investigated for initial effects, and at the lower monomer concentration (and lower $C_{tr,p}$) fewer residence times are required for M_w to reach steady state. At six residence times, simulations showed M_w was at 99% of the steady state level (67% conversion). Since Baade et al.'s experiments showed steady state occurred after six residence times and measurements were at these points, their M_w values should have been at steady state.

A third factor suggested for the M_w behavior was that the CSTR had a high degree of segregation. Chatterjee et al. computed segregation numbers and concluded segregation was not a factor, although the parameter values used are uncertain. Baade et al. had conducted HCSTR polymerizations in dilute solution ($M_0 = 1.407$ mol/L, stirrer speed 1600 rpm). In order to find out how intensively micromixed the polymerizing solution was, the degree of segregation, J_s , was determined following the method of Truong and Methot³² and Vollmerhausen³³ for homogeneous systems. An average value of the degree of segregation of 0.15 was determined in the range of conversion from 20% to 60%, where a value of 0 corresponds to maximum

mixedness and a value of 1 corresponds to complete segregation. Since Chatterjee et al. used a monomer concentration of 3.56 mol/L and a stirrer speed of 300 rpm, it is likely Chatterjee et al.'s CSTR system had a considerable degree of segregation, and that could explain why their data were much closer to the SCSTR predictions.

Concentration and Branching Effects on the MWD

As the degree of chain branching in vinyl acetate polymerization increases, the MWD becomes broader, as shown in Figure 4 for an SCSTR in suspension polymerization. In this case the polymer transfer constant is increased to increase the chain branching contribution, but the same behavior is observed with TDBP and monomer concentration. As the monomer concentration is increased in the feed, the polymer concentration at a given conversion will correspondingly increase, and more branching will occur.

A comparison of Q vs. X_m in the three reactor types, all in solution polymerization, for the conditions of Baade et al.¹ is given in Figure 5. In this case, Q_{HCSTR} is the greatest, Q_{BR} the least, and Q_{SCSTR} lies in between. This order of Q curves, decreasing in the order HCSTR, SCSTR, and BR agrees with the trends of Graessley et al.³⁻⁷ Since Graessley's initial analysis did not include initiation effects on molecular weight, the effect of changing initiator type and concentration was investigated. When the initiator concentration I_0 in the feed is increased by a factor of 5, and k_d is 100 times

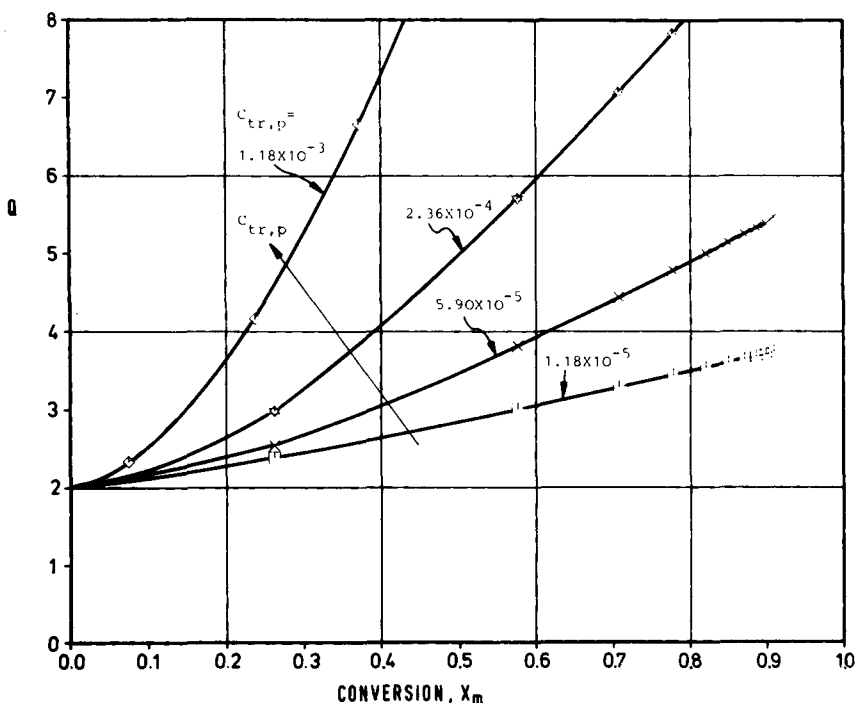


Fig. 4. The effect on Q as a function of conversion from changing the degree of chain branching, $C_{tr,p}$ in the SCSTR. Suspension polymerization is considered (kinetic parameters and concentrations from Tables IIA and IIB).

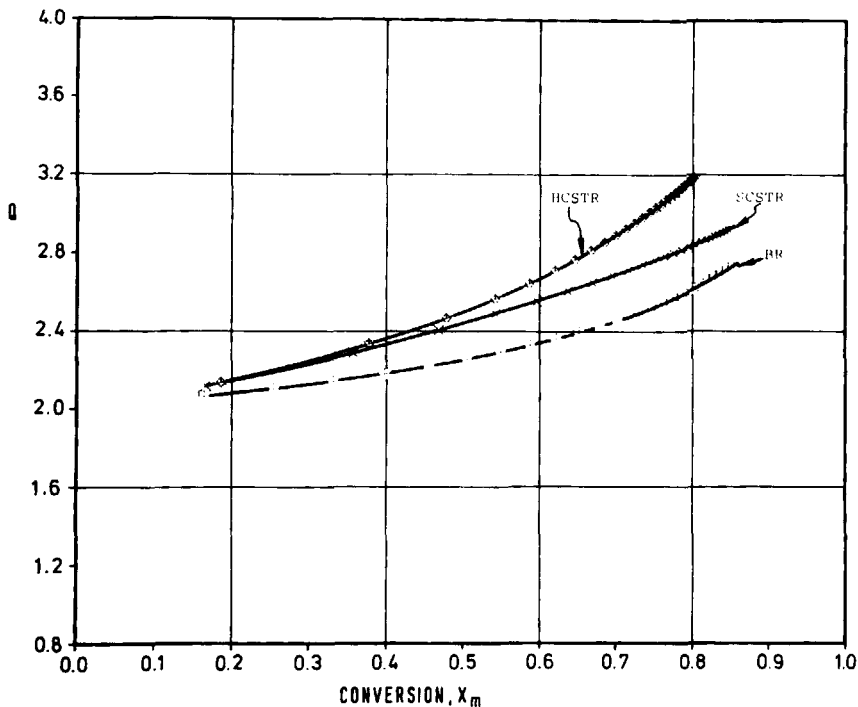


Fig. 5. A case demonstrating Q_{HCSTR} being greater than Q_{SCSTR} as conversion is increased. The parameter values used are given in Tables IIA and IIB, and all reactors are considered to be in solution.

smaller, a different order with regard to the MWD is observed (Fig. 6). In this case Q_{SCSTR} is greater than Q_{HCSTR} , with the BR having the narrowest distribution. These results demonstrate that the order of the MWD in the three reactor types is not fixed, but a function of the reactant concentrations. Figure 7 shows predictions of Q vs. X_m for the same initiator concentration and type as Figure 6, but here M_0 is increased from 1.407 to 5.0 mol/L. Now Q_{HCSTR} is above Q_{SCSTR} , implying that monomer concentration plays a significant role in the MWD breadth, and that branching affects the HCSTR more. Villermaux³⁴ has also shown that initiator type and concentration can change the MWD order in the three reactor types.

To explain why increasing the initiator concentration and decreasing k_d cause Q to be greater in the SCSTR than in the HCSTR, it is helpful to look at the probability of propagation (probability that a polymer chain will add another monomer unit versus transfer or termination) for the case of no branching³⁵:

$$\alpha_p = \frac{k_p M}{k_p M + k_{tr,m} M + k_{tr,s} S + k_t \lambda_{0t}} \quad (48)$$

or

$$\alpha_p = \frac{1}{1 + C_{tr,m} + C_{tr,s}(S/M) + N_{mw}} \quad (49)$$

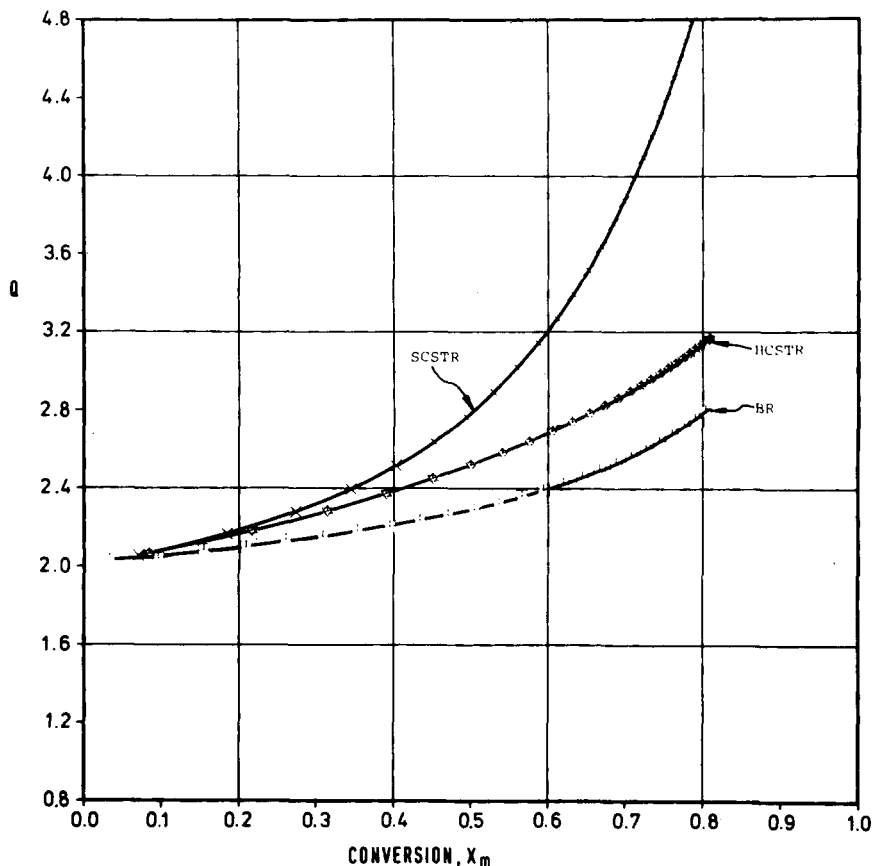


Fig. 6. A plot illustrating the effect of changing initiator concentration and decomposition rate simultaneously in the three reactor types. Here Q_{SCSTR} is greater than Q_{HCSTR} as the conversion is increased. All reactors are in solution polymerization, and $I_0 = 1.06 \times 10^{-2}$ mol/L and $k_d = 2.28 \times 10^{-6} \text{ s}^{-1}$ (5 times greater initiator concentration level and 100 times slower decomposing initiator than that used in Fig. 5). All other parameters are given in Tables IIA and IIB.

where

$$N_{mw} = (2fk_d)^{1/2} (k_t^{1/2} / k_p) (I^{1/2} / M) \quad (50)$$

The molecular weights of polymer radicals in the absence of chain branching given by

$$M_{nr} = M_{va} / (1 - \alpha_p) \quad (51)$$

$$M_{wr} = M_{va} (1 + \alpha_p) / (1 - \alpha_p) \quad (52)$$

and it is clear that changes in α_p will affect the molecular weights.

Table IV presents α_p , N_{mw} , M_{nr} , and M_n values as a function of conversion for the BR cases illustrated in Figures 5 and 6 without chain branching. In Table IVA, the time for 90% conversion is 12,100 s, while in Table IVB, where the initiator decomposes 100 times slower and is five times more

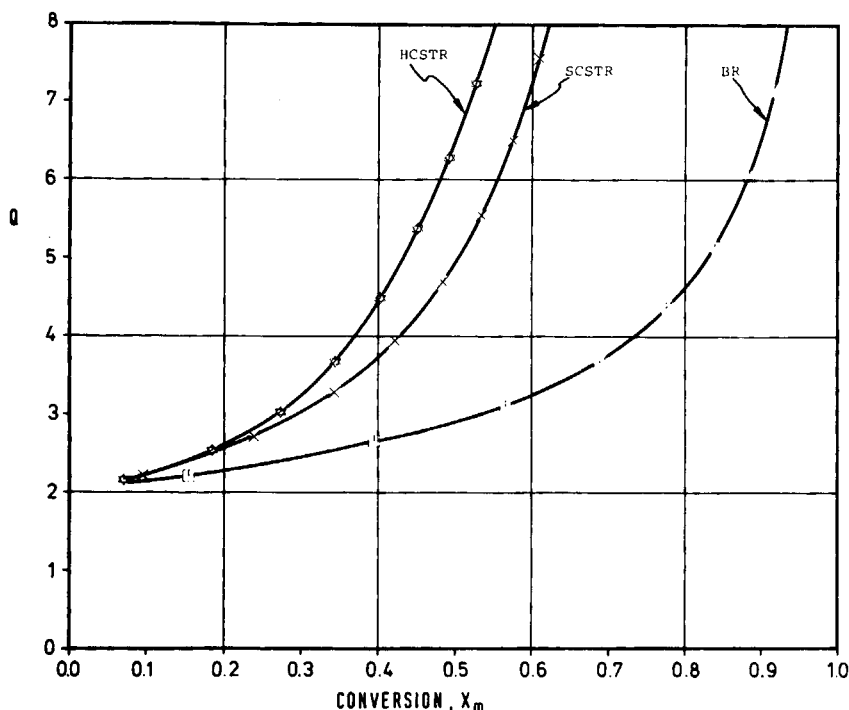


Fig. 7. The effect of increasing monomer concentration on the order of the polydispersity curves in the three reactor types in solution polymerization. The same initiator type and concentration is used as in Figure 6, $I_0 = 1.06 \times 10^{-2}$ mol/L and $k_d = 2.28 \times 10^{-6}$ s $^{-1}$, but the monomer concentration is increased from 1.407 to 5.0 mol/L. Here $S = 5.72$ mol/L, $C_{tr,p} = 1.74 \times 10^{-4}$, and all other parameters are given in Tables IIA and IIB.

concentrated, the time for 90% monomer conversion is 27,900 s. The results of Table IVA correspond to an initiator conversion of 93.7% at 90% monomer conversion, which has a half-life of 3.03×10^3 s, while Table IVB has an initiator conversion of 6.18% and 3.03×10^5 s half-life. In Table IVA,

TABLE IV
Effect of Initiator Type and Concentration on α_p , N_{mw} , M_{nr} , and M_n with Conversion

X_m	T (s)	α_p	$N_{mw} \times 10^3$	$M_{nr} \times 10^{-4}$	$M_n \times 10^{-4}$
A. $k_d = 2.285 \times 10^{-4}$ s $^{-1}$, $I_0 = 2.115 \times 10^{-3}$ mol/L					
0.10	306	0.99846	1.05	5.58	5.76
0.30	1080	0.99820	1.24	4.78	5.36
0.50	2240	0.99779	1.52	3.90	4.90
0.70	4350	0.99703	1.99	2.90	4.34
0.90	12,100	0.99503	2.46	1.75	3.62
B. $k_d = 2.285 \times 10^{-6}$ s $^{-1}$, $I_0 = 1.06 \times 10^{-2}$ mol/L					
0.10	1250	0.99925	0.260	11.4	11.8
0.30	4260	0.99910	0.334	9.58	10.9
0.50	8290	0.99884	0.465	7.44	9.79
0.70	14,500	0.99824	0.768	4.90	8.36
0.90	27,900	0.99528	2.26	1.82	6.12

the relative changes in α_p , N_{mw} , and M_{nr} are less than those in Table IVB, and hence the case in Table IVB will give a product with a broader MWD. The M_{nr} values in Table IVA decrease by a factor of approximately 3 (going from 10% to 90% conversion), while M_{nr} in Table IVB decreases by a factor of approximately 6. The total M_n in both lags behind M_{nr} .

The effect illustrated in Table IV, the changing of molecular weights with time for the BR, will not occur in the HCSTR since reaction conditions are constant. For the reactant concentrations of Figure 6 and Table IVB, Q_{BR} is 2.24 without chain branching, and 2.78 with branching at 80% conversion. In the SCSTR, Q changes from 4.25 to 5.01 when branching is added, and, in the HCSTR, Q changes from 2.00 to 3.14 at 80% conversion. The addition of chain branching causes the largest increase on Q_{HCSTR} . Although the HCSTR product is more highly branched, Q_{SCSTR} lies above Q_{HCSTR} in Figure 6 because it is also broadened by changing conditions and residence time distribution effects. When chain branching is increased, as in Figure 7 with a higher monomer concentration, the HCSTR shows even a larger branching effect, and now Q_{HCSTR} is the greatest.

Changing the degree of branching can change the MWD order in the three reactors, as demonstrated in Figures 8–10. The reactions are all in solution, using the concentrations of Chatterjee et al.³ and no TDBP is considered. Figure 8 has no polymer transfer, and the MWD order is SCSTR,

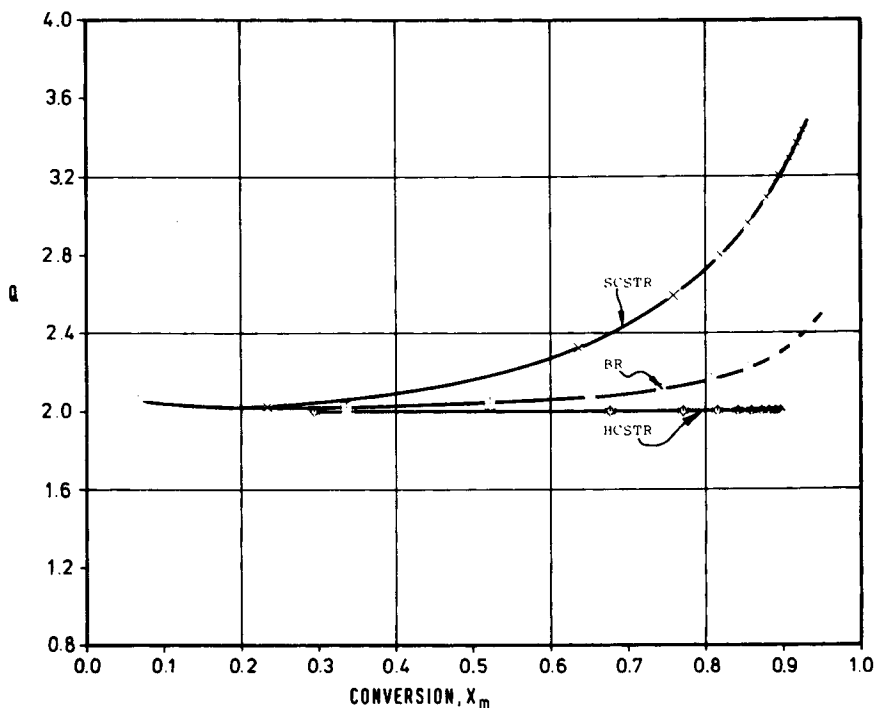


Fig. 8. Q as a function of conversion in the three reactor types, with no chain branching present, and Q decreases in the order SCSTR, BR, HCSTR. All reactors are in solution, $C_{tr,p} = C_{pd} = 0$, $M_0 = 3.56$ mol/L, $I_0 = 1.6 \times 10^{-3}$ mol/L, and other parameters are given in Tables IIA and IIB.

BR, and HCSTR, the same as reported by Tadmore and Biesenberger.¹¹ Figure 9 shows the results when $C_{tr,p}$ is increased to 5.26×10^{-5} , in which the MWD order has changed to SCSTR, HCSTR, and BR. Figure 10 demonstrates the effect of further increasing $C_{tr,p}$ to 3.16×10^{-4} , where the MWD order is now HCSTR, SCSTR, and finally BR. The effect of changing the MWD order can also arise from starting at a low monomer concentration and running the reactors at consecutively increasing monomer concentrations. This again supports the fact that transfer to polymer plays a larger role in the HCSTR, and, when the branching becomes large enough, the HCSTR will have the broadest MWD.

CONCLUSIONS

The MWD order in the three reactor types is not fixed but a function of reactant concentrations. If the reaction conditions cause a large change in the molecular weights with conversion in the BR and SCSTR, the distribution will be broadened, as in the case of a high concentration of slow decomposing initiator. This will have no effect on the MWD in the HCSTR, since reaction conditions are constant. As the monomer concentration is

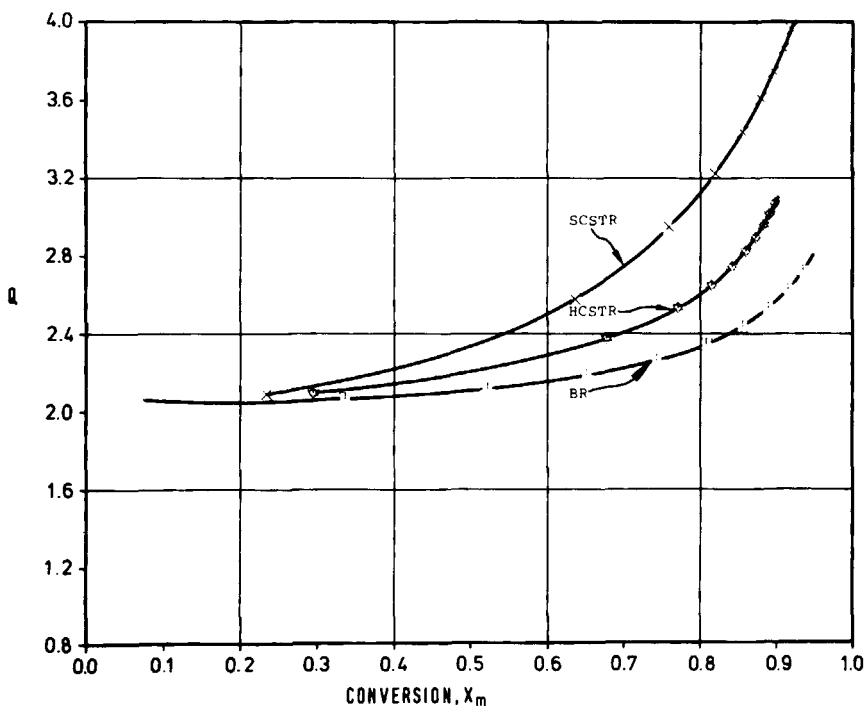


Fig. 9. Q as a function of conversion in the three reactor types, where chain branching occurs only from polymer transfer, and Q decreases in the order SCSTR, HCSTR, BR. All reactors are in solution, $C_{tr,p} = 5.26 \times 10^{-5}$, $C_{pdb} = 0$, $M_0 = 3.56$ mol/L, $I_0 = 1.6 \times 10^{-3}$ mol/L, and other parameters are given in Tables IIA and IIB.

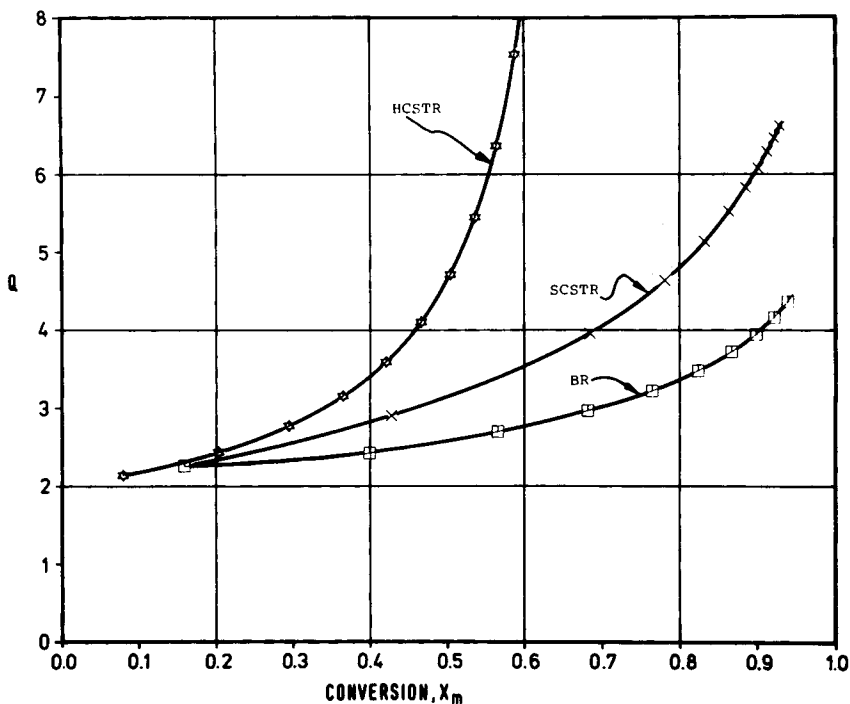


Fig. 10. Q as a function of conversion in the three reactor types, where chain branching occurs only from polymer transfer, and Q decreases in the order HCSTR, SCSTR, BR. All reactors are in solution, $C_{u,p} = 3.16 \times 10^{-4}$, $C_{pib} = 0$, $M_0 = 3.56$ mol/L, $I_0 = 1.6 \times 10^{-3}$ mol/L, and other parameters are given in Tables IIA and IIB.

increased or polymer transfer and TDBP become more important, the MWD will become broader in the HCSTR than in the BR or SCSTR.

The HCSTR and SCSTR are limiting cases, and real reactors will have MWDs between the two. Continuous suspension polymerization with little coalescence approaches an SCSTR at bulk concentrations, while solution polymerization with low monomer concentrations and conversions plus rigorous stirring will approach the HCSTR. Since the initial SCSTR monomer concentrations in this case are greater than the HCSTR, the actual SCSTR MWD will tend to be broader than that in the HCSTR.

Terminal double bond polymerization occurs between a polymer radical and a molecule with a terminal double bond, and, as with termination, two large molecular weight chains must come together. Addition of a gel effect for TDBP analogous to that of termination showed better agreement of the experimental BR and SCSTR data in the suspension polymerization cases.

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NOMENCLATURE

A	termination gel effect correlation constant (s^{-1})
B	terminal double bond polymerization gel effect correlation constant (s^{-1})
C_{pdb}	ratio of TDBP rate constant to propagation constant, dimensionless
$C_{tr,m}$	ratio of monomer transfer constant to propagation constant, dimensionless
$C_{tr,p}$	ratio of polymer transfer constant to propagation constant, dimensionless
$C_{tr,s}$	ratio of solvent transfer constant to propagation constant, dimensionless
E	residence time distribution function, dimensionless
f	initiator efficiency, dimensionless
G_{pdb}	terminal double bond polymerization gel effect factor, dimensionless
G_t	termination gel effect factor, dimensionless
I	initiator concentration (mol/L)
I_0	initial initiator concentration (mol/L)
J_s	degree of segregation, dimensionless
k_d	initiator decomposition constant (s^{-1})
k_i	initiator fragment rate constant ($L mol^{-1} s^{-1}$)
k_p	propagation rate constant, ($L mol^{-1} s^{-1}$)
k_{pdb}	terminal double bond polymerization constant ($L mol^{-1} s^{-1}$)
$k_{tr,m}$	monomer transfer constant ($L mol^{-1} s^{-1}$)
$k_{tr,p}$	polymer transfer constant ($L mol^{-1} s^{-1}$)
$k_{tr,s}$	solvent transfer constant ($L mol^{-1} s^{-1}$)
k_t	termination rate constant ($L mol^{-1} s^{-1}$)
M	monomer concentration (mol/L)
M_0	initial monomer concentration (mol/L)
M_n	number average molecular weight (g/mol)
$M_{n,b}$	concentration of polymer molecules with n monomer units and b branch points (mol/L)
$M_{n,b}^-$	concentration of polymer molecules with n monomer units, b branch points, and a terminal double bond (mol/L)
M_{nr}	number average molecular weight of polymer radicals (g/mol)
M_{va}	vinyl acetate molecular weight (g/mol)
M_w	weight average molecular weight (g/mol)
M_{wr}	weight average molecular weight of polymer radicals (g/mol)
N_{nu}	parameter group in probability of propagation, dimensionless
$P_{n,b}$	concentration of polymer radicals with n monomer units and b branch points (mol/L)
$P_{n,b}^-$	concentration of polymer radicals with n monomer units, b branch points, and a terminal double bond (mol/L)
Q	polydispersity, dimensionless
R	initiator fragment concentration (mol/L)
S	solvent concentration (mol/L)
t	time (s)
X_I	initiator conversion, dimensionless
X_m	monomer conversion, dimensionless

Greek Symbols

α_p	probability of propagation, dimensionless
θ	reaction time, dimensionless
λ_i	i th polymer radical moment (mol/L)
λ_{it}	i th total polymer radical moment (mol/L)
ν_i	i th polymer molecule moment (mol/L)
ν_{it}	i th total polymer molecule moment (mol/L)
τ	reactor residence time (s)
ϕ_s	solvent fraction relative to initial monomer concentration, dimensionless

Abbreviations

BR	batch reactor
CSTR	continuous stirred tank reactor
HCSTR	homogeneous continuous stirred tank reactor
MWD	molecular weight distribution
SCSTR	segregated continuous stirred tank reactor
TDBP	terminal double bond polymerization

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