

Simulation of the Kinetics of Styrene Polymerization

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A mathematical model for styrene polymerization, based on free-radical kinetics, accounts for changes in termination coefficient with increasing conversion by an empirical function of viscosity at the polymerization temperature. Solution of the differential equations results in an expression that calculates the weight fraction of polymer of selected chain lengths. Conversions, and number, weight, and Z molecular-weight averages are also predicted as a function of time. The model was tested on peroxide-initiated suspension polymerizations and also on batch and continuous thermally initiated bulk polymerizations.

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Bamford et al.(1) have presented the basic kinetics for free-radical polymerization of styrene, and Hamielec et al.,(2) employing Bamford's nomenclature, developed differential equations that are the starting point for the mathematical model.

The rates (in moles/litre sec) of the component reactions in the overall free-radical chain scheme are as follows:

$$\text{The rate of initiation, } I = 2 \cdot f \cdot k_d \cdot I_n + k_{ti} \cdot M^x$$

where

f = the efficiency of the initiator in starting reaction chains.

k_d = rate coefficient for decomposition of the initiator, sec^{-1}

I_n = initiator concentration in moles/litre

M = monomer concentration in moles/litre

x = exponent for thermal initiation, assumed = 3.

The rate of chain propagation of a radical of chain length

$$r = K_p \cdot M \cdot R_r^0$$

k_p = rate coefficient for propagation litre/mole sec.

R_r^0 = concentration of radicals of chain length r moles/litre.

The rate of termination of radicals of chain length

$$r = k_{tc} \cdot R_r^0 \cdot R^0 \quad (\text{Termination is assumed to be by combination only}).$$

k_{tc} = rate coefficient for termination litre/mole sec.

R^0 = total concentration of free radicals mole/litre.

The rates of chain transfer are:

$$\text{To solvent} = k_{fs} \cdot R_r^0 \cdot S$$

$$\text{To monomer} = k_f \cdot R_r^0 \cdot M$$

k_{fs} = rate coefficient for chain transfer to solvent, litre/mole sec.

S = solvent concentration, moles/litre.

k_f = rate coefficient for chain transfer to monomer, litre/mole sec.

The differential equations used in this model are the same as those presented by Hamielec.(2) The rate of change of concentration of radicals of chain length one (R_1^0) is given by

$$\frac{dR_1^0}{dt} = I - k_p \cdot M \cdot R_1^0 + (k_{fs} \cdot S + k_f \cdot M) \cdot (R^0 - R_1^0) - k_{tc} R_1^0 \cdot R^0 \quad (1)$$

The rate of change for R_2^0 and longer chains is

$$\frac{dR_r^0}{dt} = k_p \cdot M \cdot R_{r-1}^0 - k_p \cdot M \cdot R_r^0 - (k_{fs} \cdot S + k_f \cdot M) \cdot R_r^0 - k_{tc} \cdot R_r^0 \cdot R^0 \quad (2)$$

The overall rate of change of radical is

$$\frac{dR^0}{dt} = \sum_{r=1}^{\infty} \frac{dR_r^0}{dt} = I - k_{tc} \cdot (R^0)^2 \quad (3)$$

The rate of monomer consumption (polymerization rate) is given by

$$-\frac{dM}{dt} = I + k_p \cdot M \cdot R^0 + k_f \cdot M \cdot R^0 \quad (4)$$

The rate of formation of dead polymer of chain length r is

$$\frac{dP_r}{dt} = (k_{fs} \cdot S + k_f \cdot M) R_r^0 + 1/2 \cdot k_{tc} \cdot \sum_{n=1}^{r-1} R_n^0 \cdot R_{r-n}^0 \quad (5)$$

If the rate of formation of radical, I , is taken as a constant for a short period of time, Equation 3 can be integrated directly for this short period to give

$$R^0 = \sqrt{\frac{I}{k_{tc}}} \cdot \tanh(\sqrt{I \cdot k_{tc}} \cdot t) \quad (6)$$

For the polymerization of styrene, $\sqrt{I \cdot k_{tc}}$ is about 0.1 so that within a few seconds of reaction time $\tanh(\sqrt{I \cdot k_{tc}} \cdot t) \approx 1$ and for all practical purposes

$$R^0 = \sqrt{\frac{I}{k_{tc}}} \quad (7)$$

Equation 4 can be integrated by the consideration that for long chains I is negligible compared with $k_p M R^0$. The result is

$$M = M_0 \cdot e^{-\int_0^t (k_p + k_f) \cdot R^0 \cdot dt} \quad (8)$$

A further simplification can be made because $\frac{dR_r^0}{dt}$ is very nearly equal to zero, giving rise to a pseudo steady state. Under this condition the derivatives can be eliminated from Equations 1 and 2, making them algebraic. These equations give a recurring relationship between R_r^0 and R_{r-1}^0 .

$$R_1^0 = R^0 \left(\frac{k_{fs} \cdot S + k_f \cdot M + \sqrt{I \cdot k_{tc}}}{k_p \cdot M + k_{fs} \cdot S + k_f \cdot M + \sqrt{I \cdot k_{tc}}} \right) \quad (9)$$

$$R_r^0 = R_{r-1}^0 \left(\frac{k_p \cdot M}{k_p \cdot M + k_{fs} \cdot S + k_f \cdot M + \sqrt{I \cdot k_{tc}}} \right) \quad (10)$$

Now let

$$\zeta = \frac{k_p \cdot M}{k_p \cdot M + k_{fs} \cdot S + k_f \cdot M + \sqrt{I \cdot k_{tc}}} \quad (11)$$

where ζ is the probability factor for the probability that a free radical will propagate rather than enter a termination reaction.

With this definition, Equation 10 can be written

$$R_r^0 = R_{r-1}^0 \cdot \zeta \quad (12)$$

and Equation 9 becomes

$$R_1^0 = R^0 \cdot (1-\zeta) \quad (13)$$

Equations 12 and 13 can be manipulated to give

$$R_r^0 = R^0 \cdot (1-\zeta) \cdot \zeta^{r-1} \quad (14)$$

With the use of Equation 14, Equation 5 can be written

$$\frac{dP_r}{dt} = \left(k_{fs} \cdot S + k_f \cdot M \right) \cdot R^0 \cdot (1-\zeta) \cdot \zeta^{r-1} + 1/2 \cdot k_{tc} \cdot R^{02} \cdot (r-1) \cdot (1-\zeta)^2 \cdot \zeta^{r-2} \quad (15)$$

If Equation 15 is integrated and summed over all the species, we get

$$\sum_{r=1}^{\infty} P_r = \int_0^t \left[\left(k_{fs} \cdot S + k_f \cdot M \right) R^0 + 1/2 \cdot k_{tc} \cdot R^{02} \right] dt \quad (16)$$

ζ does not appear in Equation 16 because the sum of the geometric

$$\text{series} \left(\sum_{r=1}^{\infty} \zeta^{r-1} = \frac{1}{1-\zeta} \right) \text{ and } \left(\sum_{r=1}^{\infty} (r-1) \cdot \zeta^{r-2} = \frac{1}{(1-\zeta)^2} \right)$$

causes the ζ to cancel out on summation.

Other values of interest are the number weight, and z average chain lengths which can be calculated by

$$\bar{M}_n = \frac{\sum_{r=1}^{\infty} r \cdot P_r}{\sum_{r=1}^{\infty} P_r} \quad (17)$$

$$\bar{M}_w = \frac{\sum_{r=1}^{\infty} r^2 \cdot P_r}{\sum_{r=1}^{\infty} r \cdot P_r} \quad (18)$$

$$\bar{M}_z = \frac{\sum_{r=1}^{\infty} r^3 \cdot P_r}{\sum_{r=1}^{\infty} r^2 \cdot P_r} \quad (19)$$

Expressions for the summations necessary to calculate these averages can be developed in the same way as Equation 16

$$\sum_{r=1}^{\infty} r \cdot P_r = \int_0^t \left[\frac{(k_{fs} \cdot S + k_f \cdot M) \cdot R^0}{(1-\zeta)} + \frac{k_{tc} \cdot R^{02}}{2(1-\zeta)} \right] dt \quad (20)$$

$$\sum_{r=1}^{\infty} r^2 \cdot P_r = \int_0^t \left[\frac{(k_{fs} \cdot S + k_f \cdot M) \cdot R^0 \cdot (1 + \zeta)}{(1-\zeta)^2} + \frac{k_{tc} \cdot R^{02} \cdot (2 + \zeta)}{2(1-\zeta)^2} \right] dt \quad (21)$$

$$\sum_{r=1}^{\infty} r^3 \cdot P_r = \int_0^t \left[\frac{(k_{fs} \cdot S + k_f \cdot M) \cdot R^0 \cdot (1 + 4\zeta + \zeta^2)}{(1-\zeta)^3} + \frac{k_{tc} \cdot R^{02} \cdot (4 + 7\zeta + \zeta^2)}{2(1-\zeta)^3} \right] dt \quad (22)$$

The weight fraction of polymers of given chain length can be calculated from

$$W_r = \frac{r \cdot P_r}{M_o - M} \quad (23)$$

This ratio can be obtained for selected chain lengths by integrating Equation 15.

Computer Model

A digital-computer program was written to solve the equations and calculate the conversion at any time in a batch polymerization. Polymerization rates, instantaneous and cumulative molecular-weight distributions, and molecular-weight averages are also calculated at this time.

Numerical integration is performed as indicated in the previous section on Equations 8, 15, 20, 21, and 22 at constant temperature over time intervals selected by the user. Up to 10 step changes in temperature can be made in the course of a batch polymerization. Provision is made for up to five initiators (primarily for suspension polymerization); in addition thermally initiated polymerization can be calculated with or without initiators.

For initial testing of the model, values of the rate coefficients were taken from the literature; modifications were made to better fit the data as shown in Table I.

As noted by earlier investigators, a correction must be applied to the termination coefficient k_{tc} to allow for the decrease in termination rate caused by the reduction in rates of diffusion of the polymer radicals as conversion and viscosity increase. An empirical correction function was developed to correct k_{tc} for the increased viscosity at higher conversions.

$$K_{tc} \text{ (corrected)} = K_{tc} \frac{1 + c_2 \cdot \exp(\log_{10} \eta - c_1)}{1 + \exp(\log_{10} \eta - c_1)}$$

where

η = zero-shear viscosity in poises

c_1 = constant = 4

c_2 = constant = e^{-5}

At low conversions and viscosities $K_{tc} \text{ (corrected)} = K_{tc}$ the expression $1 + \exp(\log_{10} \eta - 4)$ in the denominator is the main correction to K_{tc} to make K_{tc} decrease to conform to the experimental data. Making the expression $1 + \exp(\log_{10} \eta - c_1)$ minimizes the effect of viscosity at low conversions, where viscosity is changing rapidly, but has a relatively small effect on the rates and molecular weights. The correction term in the numerator was included to moderate the effect of the denominator at very high viscosities and conversions.

The zero-shear viscosity was calculated by Hoffman (3) adapting the generalized equation of Berry and Fox (4)

Table I
Rate Coefficients for Polymerization of Styrene

Rate Coefficient	Symbol	Literature Value	Model Value	Reference
Propagation	k_p	$1.051 \times 10^7 \exp(-3557/T)$	$1.051 \times 10^7 \exp(-3557/T)$	2
Termination by combination	k_{tc}	$1.255 \times 10^9 \exp(-844/T)$	$1.255 \times 10^9 \exp(-844/T)$	2
Chain transfer to monomer	k_f	$2.31 \times 10^6 \exp(-6377/T)$	$2.14 \times 10^7 \exp(-6952/T)$	2
Initiator decomposition	k_d			
Benzoyl peroxide		$1.073 \times 10^{14} \exp(-14895/T)$	$1.712 \times 10^{15} \exp(-15924/T)$	8
t-Butyl perbenzoate		$2.25 \times 10^{15} \exp(-17500/T)$	$6.00 \times 10^{14} \exp(-17275/T)$	8
Chain transfer to				
Ethylbenzene	k_{fs}	$0.3115 \exp(-2775/T)$	$0.3115 \exp(-2775/T)$	9
Initiator efficiency	f			
Benzoyl peroxide		0.60	0.525	10
t-butyl perbenzoate		None	0.525	
Thermal initiation	k_{ti}	$1.23 \times 10^{10} \exp(-18600/T)$	$1.99 \times 10^6 \exp(-14842/T)$	11
Exponent		3.0	3.0	11

$$\log \eta - a \log(\rho \bar{M}_w) = 4.32(a - 1) - 7.5 + C$$

where η is the polymer (shear rate independent) viscosity in poises, ρ is the polymer concentration, \bar{M}_w is the weight average molecular weight of the polymer, and a is equal to 3.4 if $\rho \bar{M}_w$ is greater than 21,000 and equal to 1.0 if $\rho \bar{M}_w$ is less than 21,000. The parameter C is a parameter accounting for the temperature dependence of viscosity.

$$1/C = \alpha(T - T_0)$$

where α and T_0 are experimental parameters unique to each polymer and T is the temperature in degrees Kelvin.

The equations are independent of the nature of the solvent except where the solvent tends to promote polymer aggregation or phase separation.

$$\alpha = 5.6 \times 10^{-4} - 7.3 \log \rho$$

$$T_0 = 89.2 - 47.0 \rho + 491 \rho^2 - 229 \rho^3$$

These expressions are analytical representations of Berry's data (5), the expression for α somewhat modified to conform to experimental values for 8 percent polystyrene in toluene.

Experimental

Batch, peroxide-initiated, suspension polymerizations were run in stirred pilot plant reactors. Conversion and molecular weight (GPC) data on a typical suspension formulation run in a 15 gallon reactor are presented in Table II and compared with computer predictions. (The heatup from 90 to 122°C was approximately linear between 8 and 9 hours.)

Final conversion and molecular weight are predicted well, but intermediate conversions and molecular weights are predicted less accurately (both high under this set of conditions).

Data on a thermal batch bulk polymerization at 150°C (run in a two-litre bench-scale reactor) are presented in Table III and compared with computer predictions. Here, the computer prediction of molecular weight is good (almost independent of conversion) while the predicted conversions are slightly low. Comparison of the model predictions with thermal polymerization data of Hui and Hamielec (6) and Husain and Hamielec (7) also indicate that the

Table II

Peroxide-Initiated Suspension Polymerization-
Comparison of Computer Predictions With Pilot-Plant Results

Formulation (parts by weight)

Styrene 100

Benzoyl Peroxide 0.148

t butyl perbenzoate 0.04

Time, hours	Temperature, °C	Predicted Values			Experimental Values		
		Conversion, %	\bar{M}_N	\bar{M}_W	Conversion, %	\bar{M}_N	\bar{M}_W
0	60	0.0			0.0		
1	90	7.9	84500	141000	6.4	66800	125800
2	90	24.6	79000	127000	21.7	70500	125700
3	90	36.3	85800	140000	31.0	75900	137600
4	90	47.2	97000	175000	36.8	82100	158100
5	90	63.4	118000	279000	45.3	95700	182400
6	90	79.7	138000	378000	55.5	106500	216700
7	90	87.1	147000	408000	63.5	145100	322200
8	90	90.8	151000	406000	76.1	136100	421000
9	122						
11	122	99.90	143000	408000	99.96	127200	407200

Table III

Batch Thermal Polymerization

Pure styrene at 150°C

Time, hr.	Predicted			Experimental		
	Conversion, %	\bar{M}_N	\bar{M}_W	Conversion, %	\bar{M}_N	\bar{M}_W
0	0	-	-	0	-	-
0.08	4.3			3		
0.50	21.6			31		
0.83	31.3	116000	222000	38	122800	244000
1.25	41.3			56		
1.75	51.7			60		
2.17	60.0			74		
2.50	66.2	126000	248000	76	115600	248900

predicted conversion rates are low for thermal polymerization over the temperature range 100–230°C.

Continuous bulk, thermal polymerizations were run in a 5.1 cm jacketed pipe loop reactor with a total length at 230 cm as diagrammed in Figure 1. A gear pump circulated the high viscosity polymerization mixture at 3.8 litres per minute. The reactor was fed from one of two reservoirs by a diaphragm pump. It was operated full at all times, with the product overflowing through a back-pressure control valve before cooling and collection. The reactor was started up batchwise, until a desired conversion was obtained, then the feed was started and allowed to continue until the solids remained steady for at least one residence time. The rate of conversion per hour was calculated as follows

$$\text{Rate \% / hr} = \frac{\text{Conversion \%}}{\text{Residence time hours}}$$

In Table IV rates and molecular weights obtained under these conditions approximating steady state are compared with rates of conversion and instantaneous molecular weights from the mathematical model of the batch process, at conversions for which experimental data were available. Quite good agreement is obtained. Temperature (140 to 160°C) is the primary variable affecting both rate and molecular weight. In addition, rate is affected by conversion and the presence of ethylbenzene, and molecular weight is affected by ethylbenzene but only very slightly by conversion.

Summary

The computer program simulates the batch polymerization of styrene and has been applied to the relatively low temperature peroxide-initiated polymerization typical of suspension processes and to higher temperature bulk, thermal conditions. It has been useful in the design of new suspension processes and for more general process analysis.

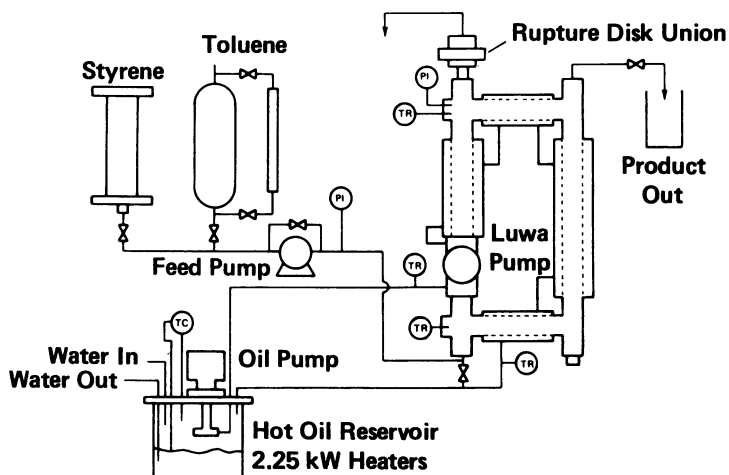


Figure 1. Continuous loop reactor.

Table IV
Continuous Bulk Thermal Polymerization of Styrene-
Comparison of Computer Prediction With Experimental Data

Temperature, °C	Ethylbenzene, %	Mineral Oil, %	Conversion, %	Predicted Values			Experimental Values		
				Rate, %/hr	\bar{M}_N	\bar{M}_W	Rate, %/hr	\bar{M}_N	\bar{M}_W
140	0	0	52	13.9	173000	341000	16.3	164100	344800
140	0	0	64	13.8	183000	365000	13.7	156200	338900
150	0	0	50	20.2	137000	272000	26.0	135600	298100
150	0	0	70	17.9	151000	302000	15.3	131600	281100
150	6	0	51	15.5	125000	248000	19.3	132000	272200
150	6	0	66.6	12.5	130000	259000	10.8	105900	233400
160	0	0	53	29.0	112000	221000	38.8	109100	236300
160	0	0	67	24.6	122000	246000	21.0	102900	235700
160	6	0	69	15.8	106000	212000	13.6	82800	190100
160	6	0	65	17.6	106000	211000	15.6	88800	200700
160	6	3	67	17.0	106000	212000	18.0	89900	193000

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Literature Cited

1. Bamford, C. H.; Barb, W. G.; Jenkins, A. D.; Onyon, P. F., "The Kinetics of Vinyl Polymerization by Radical Mechanics;" Butterworths; London, 1958.
2. Hamielec, A. E.; Hodgins, J. W.; Tebbens, K. A.I.Ch.E Journal 1967, 13, 1087.
3. Hoffman, R. D. USS Research Memorandum, Nov. 22, 1974.
4. Berry, G. C. and Fox, T. G., Adv. Polymer Sci. 1968, 5, 261-357.
5. Berry, G. C., J. Phys. Chem. 1966, 70, 1194.
6. Hui, A. W., and Hamielec, A. E., J. Appl. Polymer Sci. 1972, 16, 749-769.
7. Husain, A., and Hamielec, A. E., J. Appl. Polymer Sci. 1978, 22, 1207-1223.
8. Masson, J. C.; in "Polymer Handbook;" Wiley; New York, 1966; p. II-88.
9. Young, L. J.; Brandrup, G.; Brandrup, J. in "Polymer Handbook;" Wiley; New York, 1966, p. II-88.
10. Flory, P. J., "Principles of Polymer Chemistry;" Cornell University Press: Ithaca, NY, 1953; p. 118.
11. Platt, A. E.; Boyer, R. F. in "Encyclopedia of Polymer Science and Technology;" Wiley; New York, 1970; p. 162.

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