Polymerization of Styrene with *n*-Butyllithium in a Batch Reactor. A Mathematical Model

TAYFUN TANLAK, ABU AHMAD, MICHAEL N. TREYBIG, and RAYFORD G. ANTHONY, *Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843*

Synopsis

Sytrene was polymerized in a 0.8-liter vessel which was operated as an isothermal and a nonisothermal batch reactor. Styrene and n-butyllithium conversions were determined for different reaction times. Rate equations were developed by use of the isothermal data and then used to estimate the conversions for the nonisothermal experiments. The importance of using nonisothermal data in the development of rate equations is illustrated.

INTRODUCTION

In the design, optimization, and control of polymerization reactors, it is desirable to have a mathematical model which adequately represents the process. The objective of this work was to study the total polymerization of styrene in benzene with *n*-butyllithium in a batch reactor and develop such a model by use of experimental data. A secondary objective was to determine the effect of nonisothermal operation on the molecular weight distributions and to determine whether the rate equations developed from isothermal data adequately predicted the performance of the nonisothermal reactor.

EXPERIMENTAL

The batch reactor was a 0.8-liter Chemco vessel equipped with a marine propeller. It was instrumented in such a manner that the temperature inside the reactor was constant within a ±0.1°C. The temperature was also continuously recorded. A run was initiated by charging benzene and styrene, heating this mixture to the desired reaction temperature, and then charging *n*-butyllithium. After the run began, samples were taken at specified times. The styrene conversion was determined gravimetrically, and the molecular weights and distributions were determined by use of gel permeation chromatography. A modified form of Smith's method[26] was used to reduce the GPC data. Initiator conversions were then determined by use of the number-average molecular weight and the styrene conversions.

The nonisothermal experiments were nearly adiabatic. The heat loss from

the reactor when operated as a nonisothermal vessel could be represented by the equation

$$-\frac{dT}{dt} = k \ (T - T_a)$$

where $k = 0.0158$ min^{-1}. However, in the calculations for the nonisothermal runs, the actual temperature inside the reaction vessel was used.

Additional experimental details are presented by Cox[1] and Tanlak.[2] The initial conditions for the isothermal runs are presented in Table I. Experimental conversions and average molecular weights are presented in Tables III through VII.

MODEL DEVELOPMENT

The polymerization of styrene with n-butyllithium in benzene is a complex system of reactions. These reactions consist of association of butyllithium with itself and with poly(styryllithium) as well as the association of poly(styryllithium) with itself.[3-15] The stoichiometry of these reactions, however, are represented as

Initiation

$$I + M \rightarrow P_1$$

Propagation

$$P_j + M \rightarrow P_{j+1} \qquad j = 1,2,3, \ldots$$
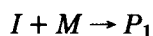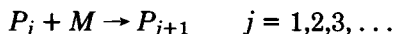
The reactions are terminated by use of an agent such as water or methyl alcohol.

INITIATION REACTION

Rate equations for the initiation reactions of the form

$$R_i = k_i I^n M \qquad \tfrac{1}{6} \le n \le 1 \tag{1}$$

have been proposed by Margerison and Newport,[10] Lenz,[8] Timm and Kubicek,[7] and Hsieh.[9] If a pseudo-time τ is defined, eq. (1) can be combined with the material balance for a batch reactor to obtain

TABLE I
Initial Conditions

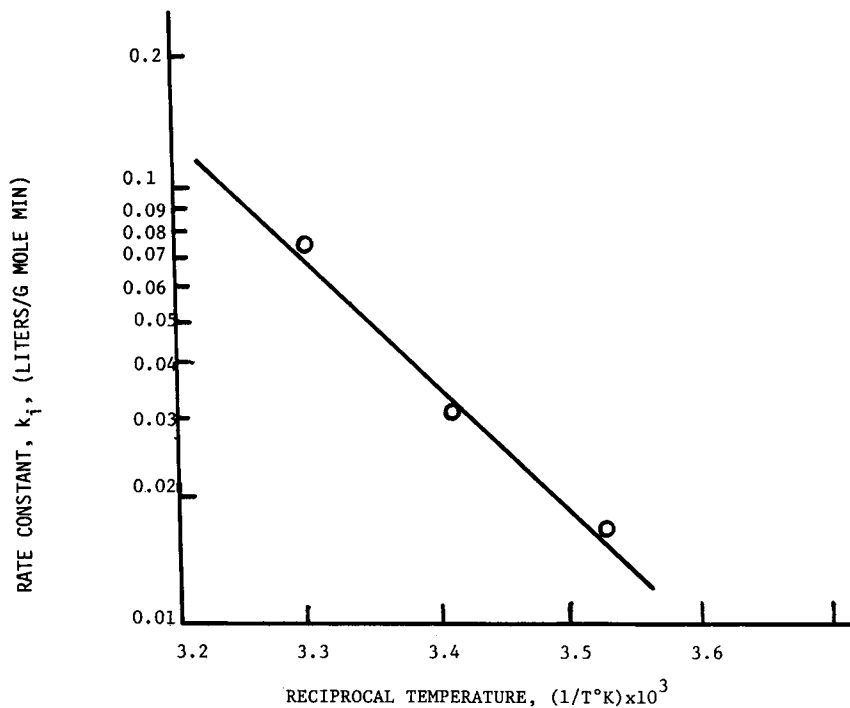| Run no.	Temperature, °C	Initial monomer concentration, moles/l.	Initial initiator concentration, moles/l.
2	20	0.983	0.00983
3	20	0.984	0.0108
5	30	0.808	0.0161
6	10	2.009	0.0049
7	20	1.244	0.00835

Fig. 1. Arrhenius plot for first-order initial initiator rate.

$$I^{1-n} - I_0^{1-n} = (n - 1)k\tau \qquad n \neq 1 \tag{2}$$

where

$$\tau = \int_0^t M dt. \tag{3}$$

For $n = 1$, $-\log_e I/I_0 = k\tau$. The τ value is obtained from the experimental data by graphically integrating the styrene concentration–time curve. Several values of n were tried, and none gave satisfactory results. Therefore, the experimental conversions of initiator for each experiment were curve fitted by use of a hyperbola.[16] The rate of initiation R_I was determined by differentiating this function. The rate R_I was also determined by graphical differentiation[17] of the initiator conversion–time curves. Good agreement was obtained between the rates obtained in this manner.

Once the rates as a function of concentration were obtained, a rate equation which included a term for an autocatalytic initiation reaction was considered because Bywater et al.[15] and Landon et al.[19] suggest that the initiation reactions for polymerization of styrene in cyclohexane with n-butyllithium are very complex and include an autocatalytic step. Porter et al.[23] have obtained similar results for polymerization of isoprene in hexane with n-butyllithium. As suggested by Porter et al.,[23] these equations may be represented as

$$R_I = k_i[f_1(I) + f_2(I,P_T)]M$$

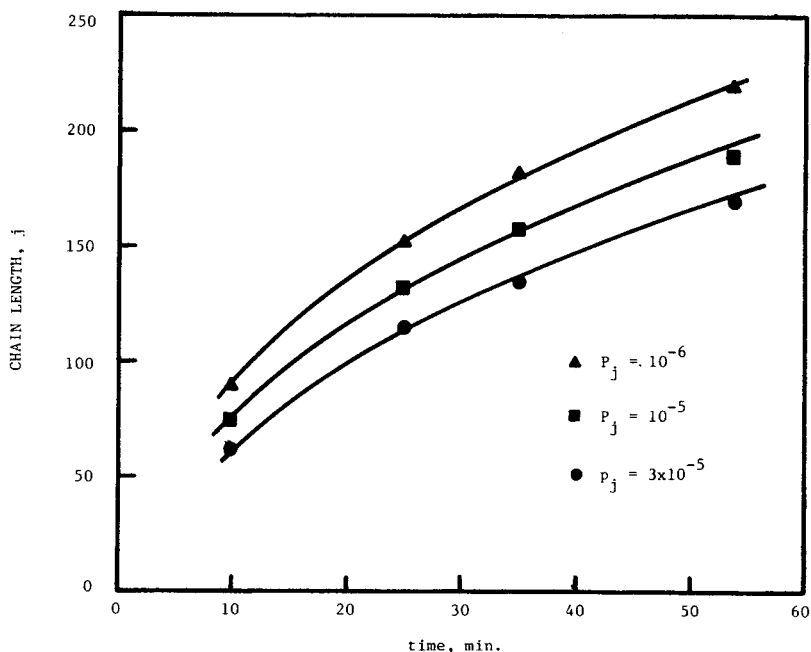To test the applicability of an autocatalytic initiation reaction, graphs which

Fig. 2. Characteristic curves, run 2.

represent the equation

$$\frac{R_I}{I^n M} = k_i + k_2 P_T \tag{4}$$

were prepared. Values of n of $1/6$, $1/3$, and 1 were used. From the intercept, $P_T = 0$, the value of k_i is obtained. If k_i fits an Arrhenius equation for a given value of n, the initial rate was determined. Figure 1 illustrates the Arrhenius plot for the case $n = 1$. The values of k_i obtained for other values of n gave unsatisfactory fits for the Arrhenius plots. Hsieh[4] has also reported values for $n = 1$ for n-

TABLE II
Initiation and Propagation Rate Constants

Con- stant	Definition	Values			Units
		10°C	20°C	30°C	
k_i	$9.4 \times 10^6 \times e^{-5700/T}$	0.0171	0.0321	0.0637	(liter)/[(g-mole)(min)]
ϕ	$3.18 \times 10^{-3} \times e^{6100/T}$	7.65×10^6	3.49×10^6	1.76×10^6	(liter)^4/[(g-mole)^4 min]
k_p	$6.2 \times 10^{12} \times e^{-7900/T}$	5.67	12.11	24.64	(liter)/[(g-mole)(min)]
K_P	$3.18 \times 10^{38} \times e^{-27600/T}$	1.4×10^{-4b}	3.92×10^{-3}	8.67×10^{-2}	(g-mole)/(liter)

a T is in degrees Kelvin.

b This value was not used to calculate the monomer conversion or number- and weight-average molecular weights. A value of $K_p = 8.67 \times 10^{-3}$ was used. Please see discussion in conclusions.
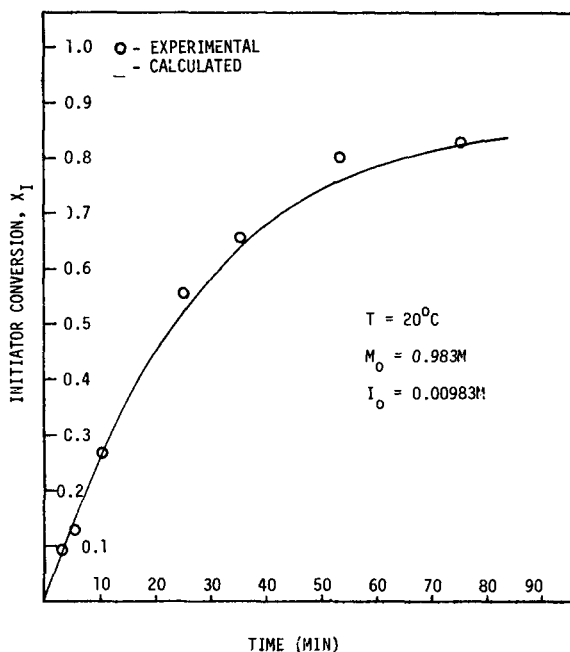
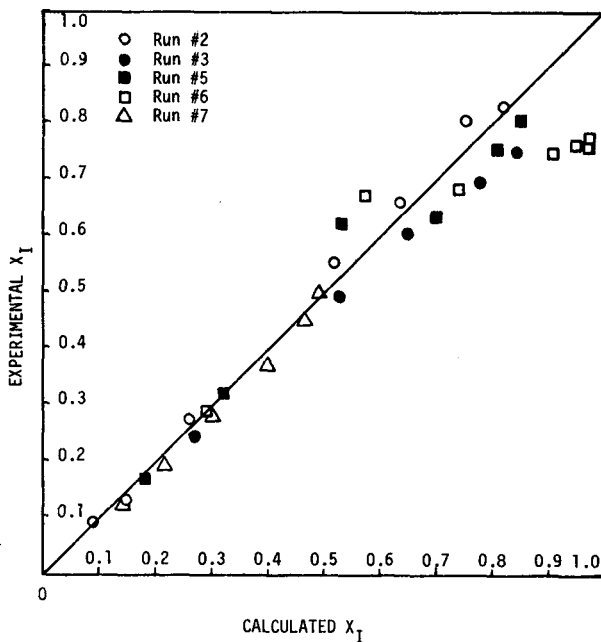Fig. 3. Variation of n-butyllithium conversion for run 2.

Fig. 4. Comparison of experimental and calculated n-butyllithium conversions.

butyllithium polymerizations of styrene in toluene and cyclohexane at low initiator conversions.

The order with respect to polymer concentration, P_T, and the value of k_2 was obtained by nonlinear regression analysis. The differential equation
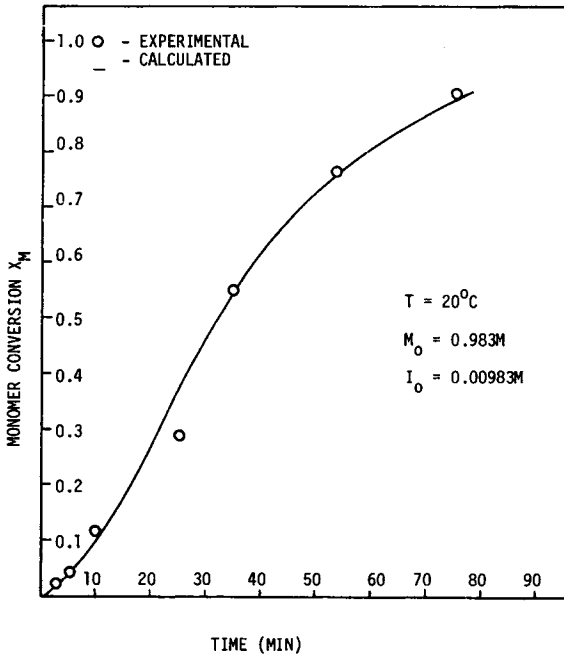
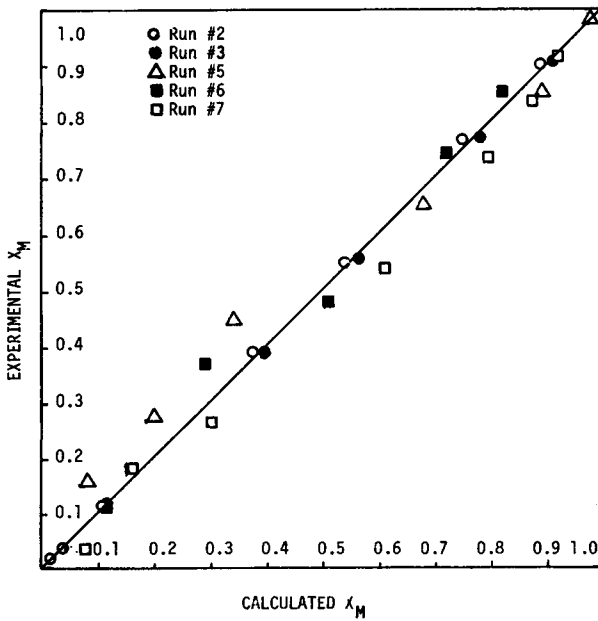Fig. 5. Variation of styrene conversion from run 2.

Fig. 6. Comparison of experimental and calculated styrene conversions.
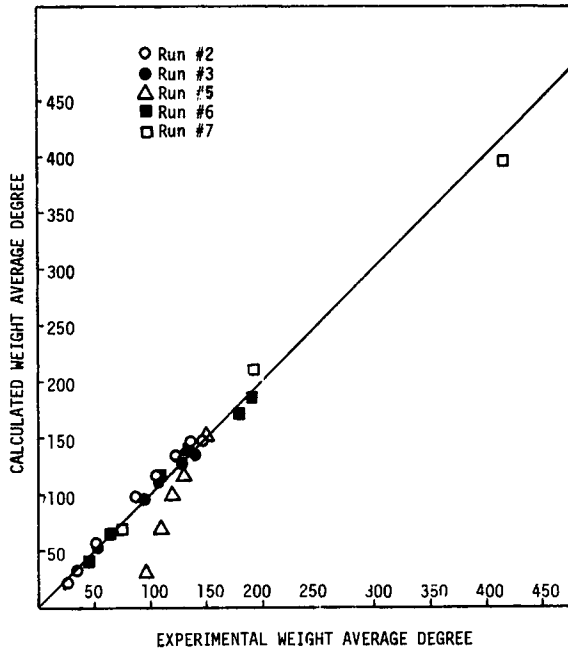
Fig. 7. Comparison of calculated and experimental weight-average degree of polymerization.
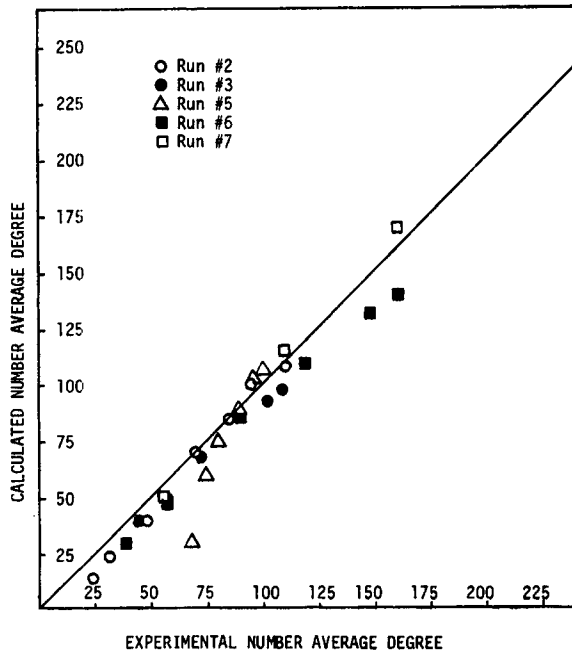

Fig. 8. Comparison of calculated and experimental number-average degree of polymerization.

TABLE III
Experimental and Calculated Results for Run 2[a]

Time, min	X_I	X_M	$\overline{D}_n$	$\overline{D}_w$	$\overline{D}_w/\overline{D}_n$
		Experimental			
3.1	0.090	0.022	23.9	26.4	1.10
5.3	0.131	0.041	31.3	35.6	1.14
10.0	0.269	0.115	42.7	50.8	1.19
25.0	0.553	0.388	70.1	86.0	1.31
35.1	0.655	0.551	84.2	104.7	1.24
53.6	0.801	0.766	95.6	123.1	1.28
75.3	0.825	0.908	110.0	136.4	1.24
		Calculated			
3.1	0.090	0.015	16.1	22.0	1.37
5.1	0.144	0.034	23.9	32.6	1.37
10.1	0.261	0.105	40.0	54.6	1.37
25.1	0.519	0.374	72.1	98.7	1.37
35.1	0.634	0.539	85.0	116.6	1.38
53.1	0.756	0.752	99.4	135.8	1.36
75.1	0.820	0.890	108.6	147.1	1.35

[a] $T = 20°C$; $M_0 = 0.983M$; $I_0 = 0.00983M$.

TABLE IV
Experimental and Calculated Results for Run 3[a]

Time, min	X_I	X_M	$\overline{D}_n$	$\overline{D}_w$	$\overline{D}_w/\overline{D}_n$
		Experimental			
9.8	0.239	0.117	44.4	52.9	1.19
25.0	0.493	0.392	72.3	90.5	1.25
35.0	0.600	0.556	84.2	107.6	1.28
53.4	0.688	0.768	101.5	128.3	1.29
75.1	0.756	0.907	109.2	139.9	1.28
		Calculated			
10.1	0.262	0.112	38.9	53.3	1.37
25.1	0.529	0.395	68.0	94.4	1.39
35.1	0.653	0.565	78.8	110.2	1.40
53.1	0.782	0.778	90.6	126.4	1.39
75.1	0.845	0.908	97.9	135.3	1.38

[a] $T = 20°C$; $M_0 = 0.984M$; $I_0 = 0.0108M$.

$$I^0 \frac{dX_I}{dt} = [k_i + k_2 P_T^a]IM$$

was numerically integrated, and the sum of squares of

$$\sum(X_{I\,cal} - X_{I\,exp})^2 \qquad (5)$$

was minimized by using direct search as proposed by Hooke and Jeeves.[18] The use of these procedures yielded a rate equation of the form

$$R_I = k_i(1 + \phi P_T^3)IM \qquad (6)$$

and the rate constants presented in Table II.

TABLE V
Experimental and Calculated Results for Run 5[a]

Time, min	X_I	X_M	$\overline{D}_n$	$\overline{D}_w$	$\overline{D}_w/\overline{D}_n$
		Experimental			
2.7	0.123	0.158	64.3	94.7	1.47
4.9	0.193	0.280	73.0	107.9	1.48
8.1	0.282	0.448	79.8	117.7	1.47
13.0	0.372	0.656	88.3	129.0	1.46
20.1	0.448	0.848	95.0	135.6	1.43
30.6	0.499	0.986	99.2	144.2	1.45
		Calculated			
3.05	0.140	0.084	37.9	51.2	1.35
5.05	0.215	0.199	55.8	75.4	1.35
8.05	0.304	0.340	75.1	101.9	1.35
13.05	0.401	0.683	92.8	127.2	1.37
20.05	0.465	0.891	102.4	141.5	1.38
30.05	0.490	0.979	106.0	147.0	1.38

[a] $T = 30°C; M_0 = 0.808M; I_0 = 0.0161M.$

TABLE VI
Experimental and Calculated Results for Run 6[a]

Time, min	X_I	X_M	$\overline{D}_n$	$\overline{D}_w$	$\overline{D}_w/\overline{D}_n$
		Experimental			
10.1	0.285	0.039	56.0	74.5	1.33
25.1	0.669	0.179	109.9	135.1	1.23
40.1	0.681	0.265	159.4	193.2	1.21
80.1	0.738	0.542	301.4	332.3	1.10
120.2	0.756	0.734	398.4	414.0	1.05
150.3	0.768	0.833	444.7	463.6	1.04
180.8	0.744	0.909	500.6	515.4	1.03
		Calculated			
10.2	0.292	0.075	52.0	69.0	1.33
25.2	0.572	0.159	114.0	147.8	1.29
40.2	0.740	0.301	166.7	211.1	1.27
80.2	0.915	0.613	274.5	328.2	1.19
120.2	0.956	0.795	340.5	393.9	1.16
150.2	0.968	0.874	369.9	422.5	1.14
180.2	0.973	0.922	388.4	440.3	1.13

[a] $T = 10°C; M_0 = 2.009M; I_0 = 0.0049M.$

PROPAGATION REACTION

The rate of propagation has been presented by Edgar et al.[3] as being of the form

$$R_p = \frac{k_p P_T M}{\frac{1}{2} + \sqrt{\frac{1}{4} + (2P_T/K_p)}} = \alpha P_T M \tag{7}$$

which reduces for large concentrations of polymer to

$$R_p = k' \sqrt{P_T} M \tag{8}$$

where

$$\alpha = \frac{k_p C_T}{P_T} = \frac{k_p}{\frac{1}{2} + \sqrt{\frac{1}{4} + (2P_T/K_p)}} \quad \text{and} \quad k' = k_p \sqrt{\frac{K_p}{2}}.$$

Equation (8) is the form reported by most investigators.[4,5,6,8-15]

Landon and Anthony[19] and Timm and Kubicek[7] have demonstrated two techniques for evaluating the equilibrium constants and absolute propagation constant for these reactions. Landon et al. minimized the sum of squares of deviation for monomer conversions and weight-average molecular weights using nonlinear regression analysis. Timm and Kubicek utilized the method of characteristics and the continuous variable assumption to solve the differential equations for the propagation reactions. They then plotted their data to obtain the characteristic curves. Their experiments were conducted in the absence of initiation. The procedure utilizing the method of characteristics is as follows:

The propagation material balances are as follows:

$$\frac{dP(1)}{dt} = R_I - \alpha P(1)M \tag{9}$$

with $P(1) = 0$ at $t = 0$, and

$$\frac{dP}{dt} + \alpha M \frac{dP}{dj} = 0 \qquad j > 1 \tag{10}$$

The solution[19] of eq. (10) by the methods of characteristics is

$$P(j(t),t) = P_1(t_0) \tag{11}$$

and

$$j(t) = 1 + \int_{t_0}^{t} \alpha M dt. \tag{12}$$

TABLE VII
Experimental and Calculated Results for Run 7[a]

| Time, min	X_I	X_M	$\overline{D}_n$	$\overline{D}_w$	$\overline{D}_w/\overline{D}_n$
			Experimental		
5.0	0.165	0.042	38.0	44.3	1.16
9.6	0.320	0.118	54.9	66.4	1.21
21.9	0.618	0.372	89.6	112.0	1.25
33.6	0.626	0.482	114.5	142.4	1.24
50.0	0.752	0.745	147.5	177.8	1.21
63.5	0.798	0.853	159.1	189.9	1.19
			Calculated		
5.1	0.178	0.036	29.8	40.6	1.36
10.1	0.318	0.108	50.4	68.3	1.35
20.1	0.527	0.287	81.3	109.4	1.34
33.1	0.698	0.509	108.6	144.8	1.33
50.1	0.811	0.718	131.8	174.0	1.31
63.1	0.854	0.820	143.2	185.5	1.29

a $T = 20°C; M_0 = 1.244M; I_0 = 0.00835M.$
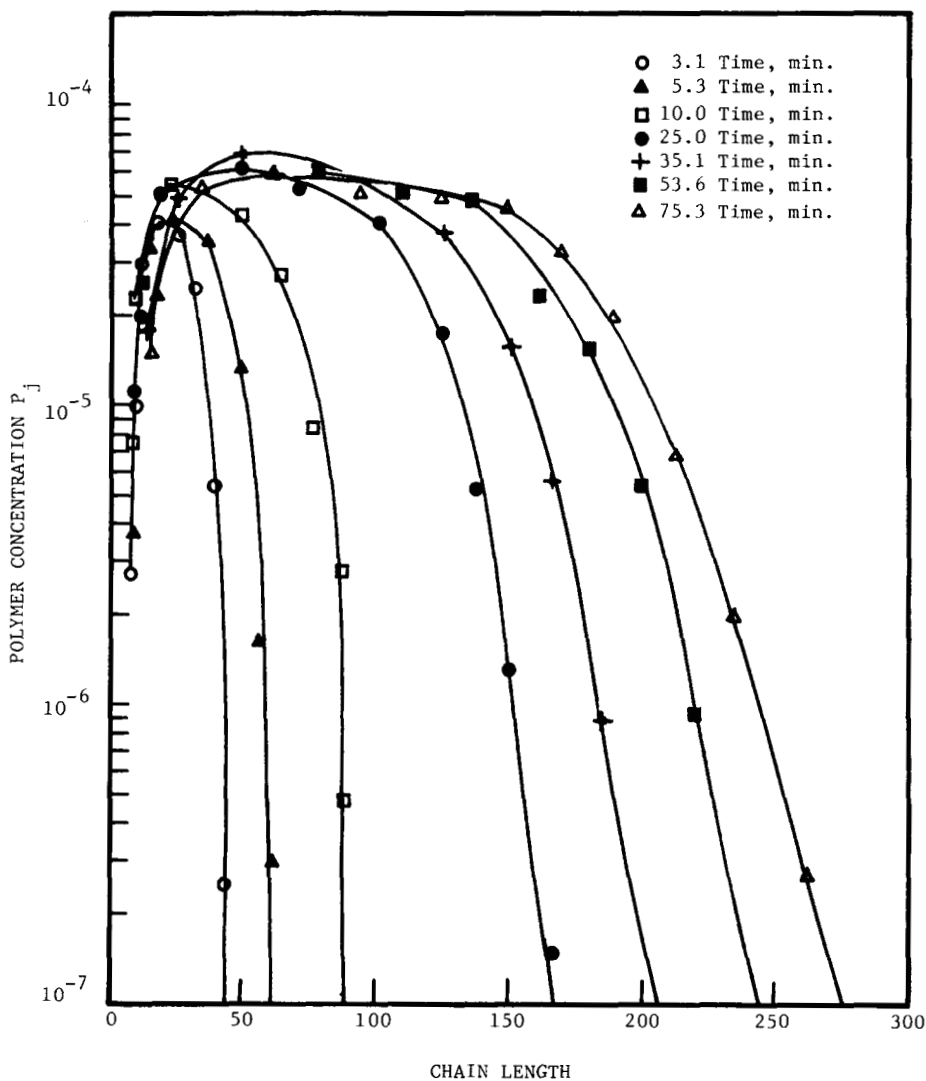
Fig. 9. Growth of polymer concentration for run 2, T = 20°C, M_0 = 0.983, I_0 = 0.00983 M.

These equations, even in the presence of initiation reactions, predict a set of characteristic curves which are parallel. Characteristic curves may be obtained from the experimental distributions by holding P_j = constant and reading j from the distributions for each sample. Plots of molar concentrations P_j of 10^{-6}, 10^{-5}, and 3×10^{-5} obtained from run 2 are illustrated in Figure 2. The most apparent feature of these curves is that they are not exactly parallel. This may be due to two factors. First, the GPC columns tended to treat all molecules less than ten units long as if they had a chain length of ten. Secondly, the association reaction may not be at equilibrium as assumed by the above mechanism. In any event, the curve for $P_j = 10^{-5}$ was used to evaluate the slope αM. Then, α was linearized as was done by Timm and Kubicek[7] to the form
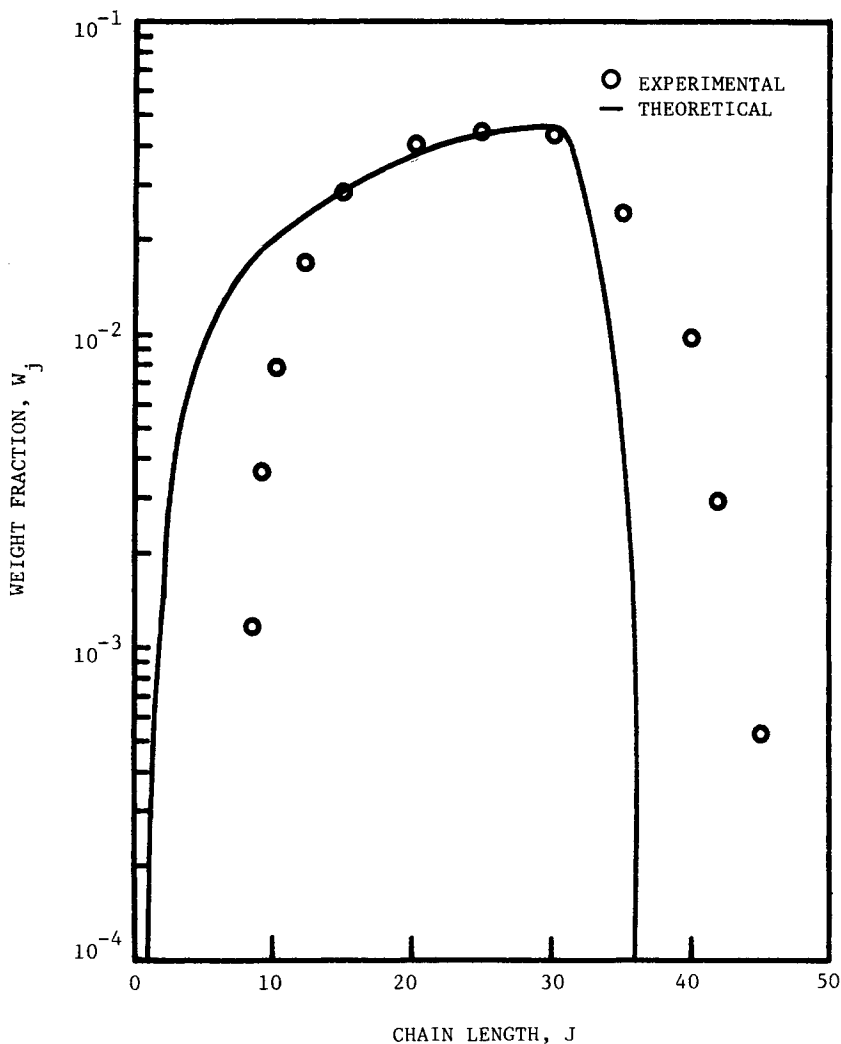
Fig. 10. Molecular weight distribution at 3.1 min for run 2.

$$\frac{1}{\alpha} = \frac{1}{k_p} + \left(\frac{2}{k_p^2 K_p}\right) \alpha P_T.$$

The values of k_p and K_p were obtained from this equation and used as first guesses in the nonlinear regression as proposed by Landon et al. The k_p and K_p values obtained by this procedure are presented in Table II.

DISCUSSION OF RESULTS

By utilizing the rate equations developed above, the styrene and n-butyllithium conversions, molecular weights, and molecular weight distributions were
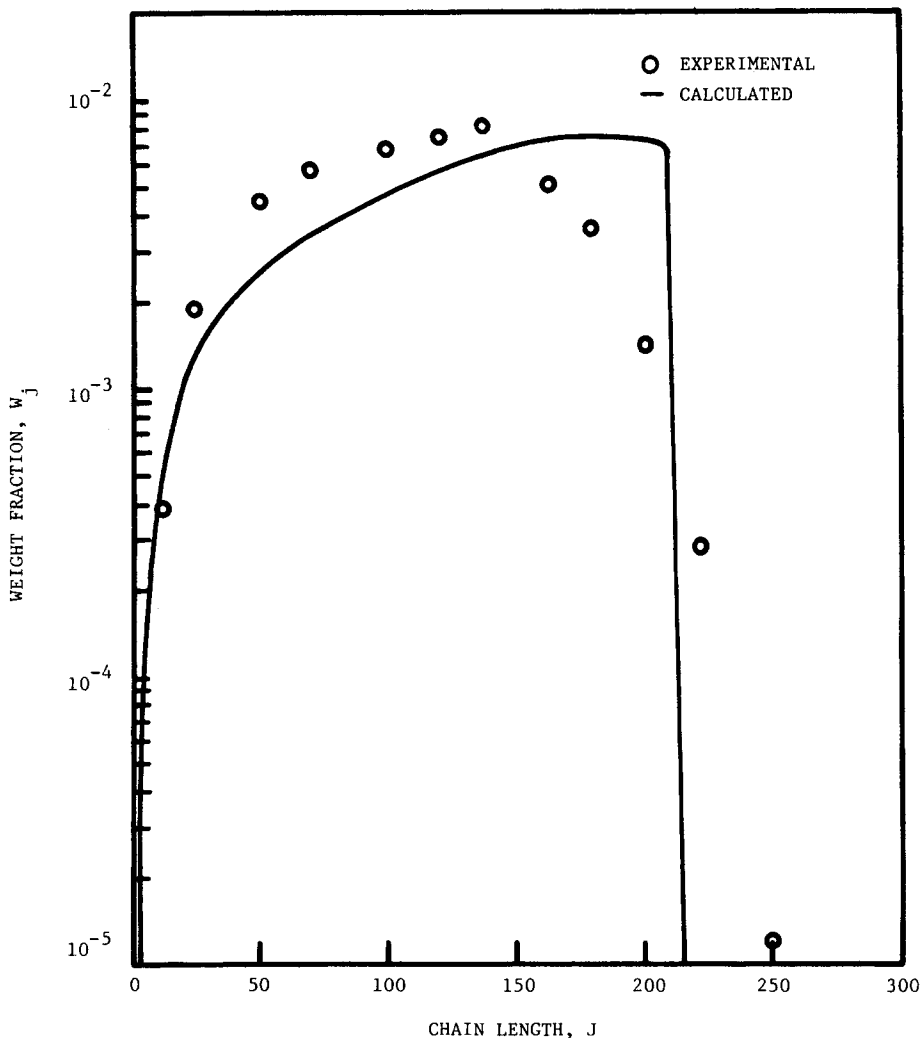
Fig. 11. Molecular weight distribution at 53.6 min for run 2.

calculated. A typical initiator–time curve is shown in Figure 3. Experimental conversions are compared with the calculated values for all runs in Figure 4. Typical styrene conversions and a comparison of calculated and experimental conversion for all runs are illustrated in Figures 5 and 6. The average molecular weights were calculated by use of the first and second moments of the distributions.[23,24]

Deviations between experimental and calculated values are illustrated in Figures 7 and 8. Calculated conversions and molecular weights are presented in Tables III through VII. Typical experimental distributions are illustrated in Figures 9, 10, and 11. The theoretical molecular weight distribution presented in Figures 10 and 11 were calculated by use of the method of characteristics.
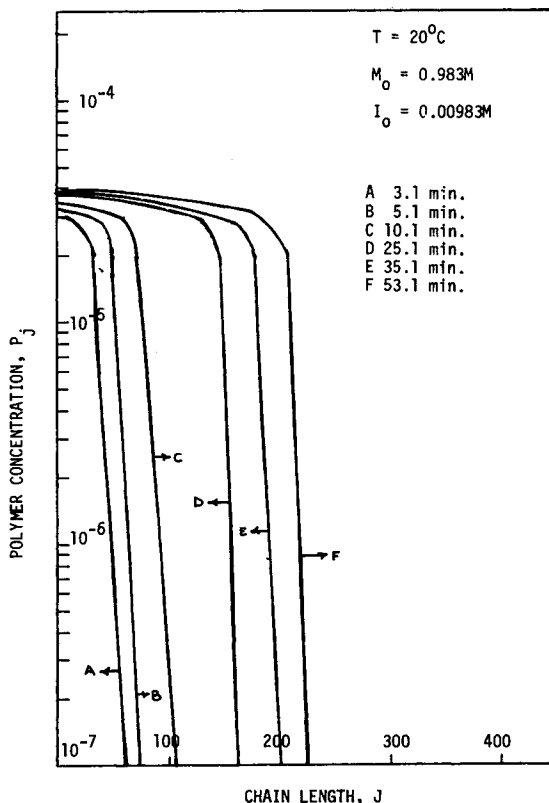
Fig. 12. Growth of calculated polymer concentration for run 2.

Distributions are calculated much faster by use of the method of characteristics than by the procedure used by Landon et al.[19]   A calculated molar distribution for run 2 is illustrated in Figure 12.

The molar distribution obtained for run 6 is illustrated in Figure 13.   After the third sample all of the initiator appears to be consumed and only propagation is occurring.   It appears that impurities were injected into the system while obtaining the third sample.   These impurities (probably air or water) reacted more rapidly with initiator than with polymer.   Hence, the presence of only the propagation reaction should be detectable by use of GPC.

Results from the nonisothermal experiments are presented in Figures 14, 15, 16, and 17.   The initial concentrations for these runs were the same as run 2.   The initial temperature was 24°C, and the temperature profile for runs 9 and 10 is illustrated in Figure 14.   Figure 15 illustrates the experimental conversions, the conversions calculated by use of the constants obtained in this work, and the constants reported by Timm.[22,25]   The experimental molar and weight distributions are illustrated in Figures 16 and 17.   One notes no substantial change in these distributions when compared to those for run 2.   Reaction times for high conversions of styrene were, however, reduced by a factor of 3.
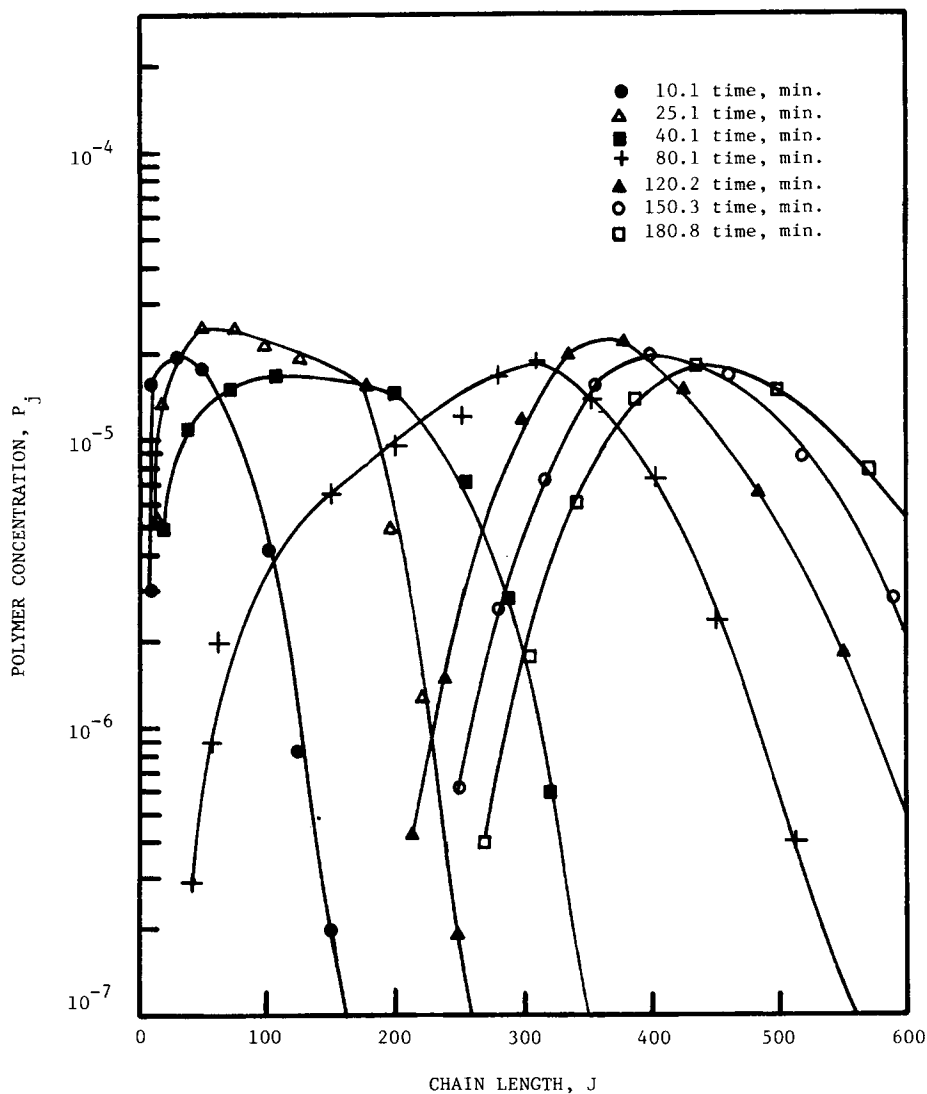
Fig. 13. Growth of polymer concentration for run 6, T = 10°C, M_0 = 2.009M, I_0 = 0.0049M.

CONCLUSIONS

A mathematical model has been developed for the batch polymerization of styrene in benzene with n-butyllithium. The use of nonisothermal data indicates a need for further refinement of the rate constants for the propagation reactions. The calculated average molecular weights and conversion of initiator and monomer were in good agreement with the experimental data.
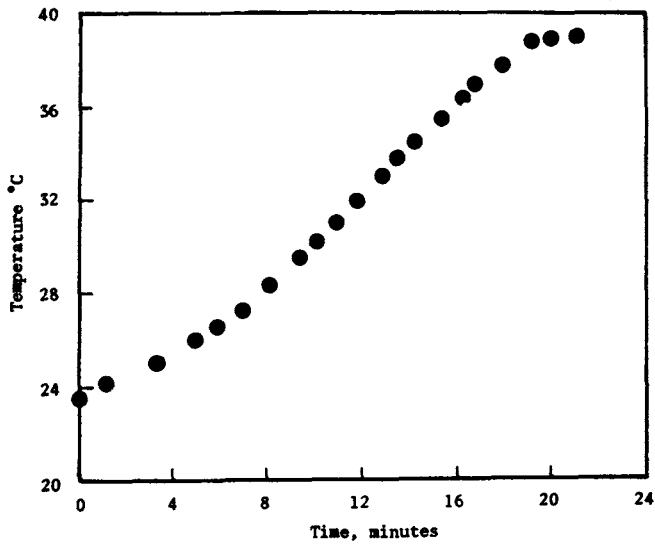
Fig. 14. Nonisothermal batch reactor, runs 9 and 10.

Notations

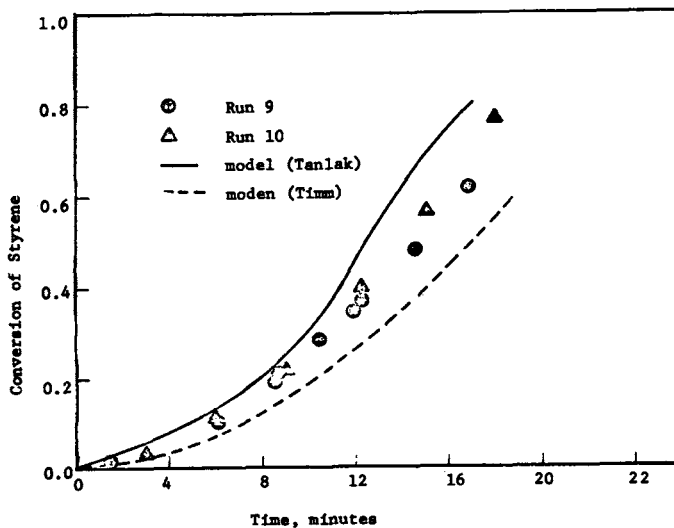|	
$\overline{D}_w$	weight-average degree of polymerization
$\overline{D}_n$	number-average degree of polymerization
GPC	gel permeation chromatograph
I_0	initial initiator concentration, g-moles/l.
I	initiator concentration at any time t
j	polymer chain length
k_I	absolute initiation rate constant

Fig. 15. Conversion of styrene for nonisothermal runs 9 and 10.
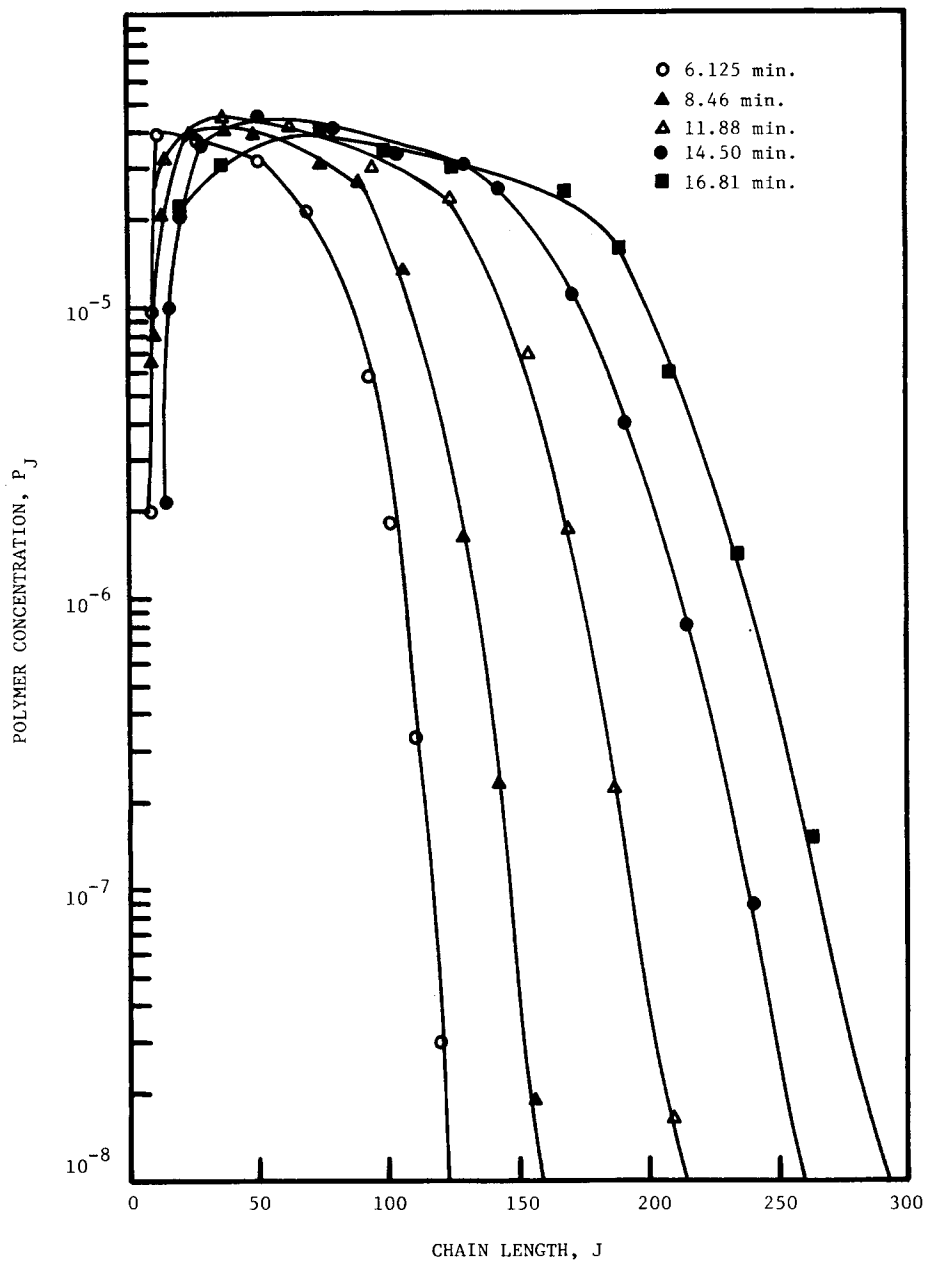
Fig. 16. Molar distributions for nonisothermal run 9.

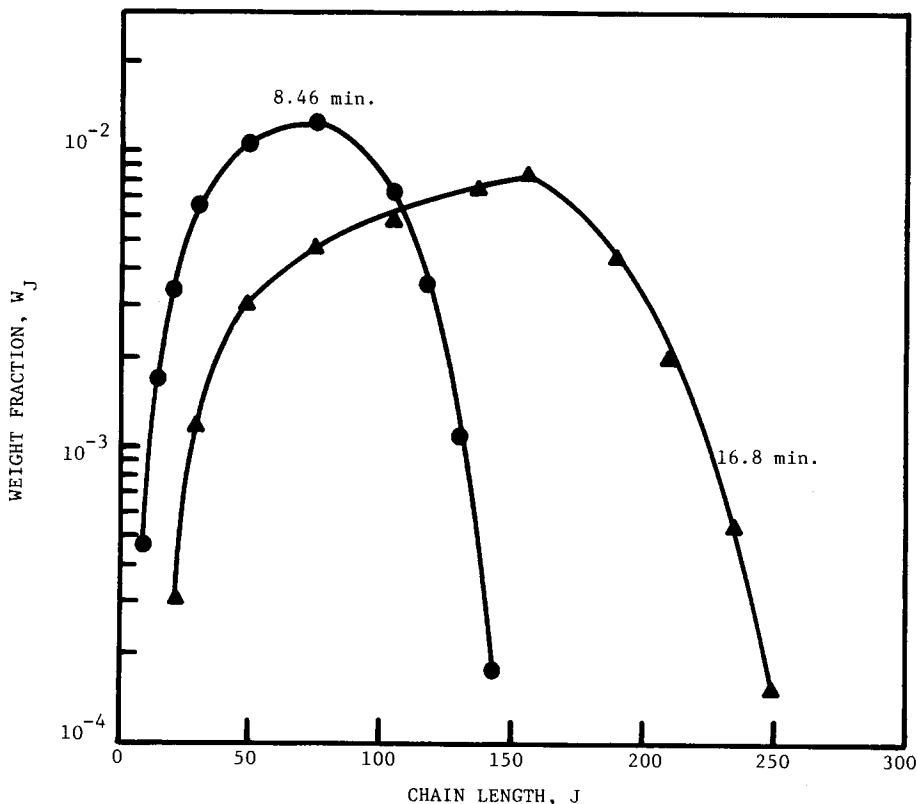| k_a | autocatalytic rate constant for initiation |
k_p	absolution propagation rate constant
K_p	equilibrium constant for polymer association
M_0	initial monomer concentration, g-moles/l.

Fig. 17. Molecular weight distribution, nonisothermal run 9.

M	monomer concentration at any time t
$\overline{M}_n$	number-average molecular weight
$\overline{M}_w$	weight-average molecular weight
$\overline{M}_w/\overline{M}_n$	heterogeneity index
n	order of reaction
P_j	concentration of total polymer of length j, g-moles/l.
$P_T = I_0 X_I$	concentration of total polymer, g-moles/l.
R_I	rate of initiation
t	time, min
V	elution volume, ml
W_j	weight fraction of polymer length j
X_I	initiator conversion
X_M	monomer conversion

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