A Mathematical Model for Polymerization of Isoprene with n-Butyllithium in Benzene

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Synopsis

Isoprene was polymerized in batch reactors by use of bottle polymerization techniques at 20°, 30°, and 40°C at concentrations from 1 to 5 molar. Isoprene and n-butyllithium conversions and molecular weight distributions were determined for different reaction times. Rate equations for the initiation and propagation reactions are presented. The importance of the association reactions in obtaining a narrow molecular weight distribution is illustrated.

SCOPE AND SIGNIFICANCE

In the design, optimization, or 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 isoprene in benzene with n-butyllithium and develop such a model by use of the experimental data. A secondary objective was to gain an insight as to the effect of the association reactions on the molecular weight distribution. This system was chosen because this process produces polyisoprene with high cis-1,4 unsaturation. *Heva* natural rubber has a cis content of nearly 100%.

EXPERIMENTAL

Six runs consisting of 32 samples were conducted in batch reactors at 20°, 30°, and 40°C. At least two runs were conducted at each temperature. Initial conditions are listed in Table I. The isoprene was double distilled and refluxed over sodium ribbon before use. Thiophene-free benzene supplied by the Fisher Scientific Company was stored for several days over sodium ribbon before use. n-Butyllithium was purchased from Foote Mineral Company in a 1.6 molar solution of benzene. This solution was diluted in benzene to approximately 0.3 molar and analyzed by use of disulfide cleavage and subsequent titration with silver nitrate. This procedure has been presented by Koltoff and Harris[1] and Uraneck et al.[2] The polymerization bottles were dried and rinsed with butyllithium solution and rerinsed with purified benzene before use. Numerous precautions

TABLE I
Initial Conditions

Run no.	Temperature, °C	Scavenger level, mmoles BuLi/100 g	Initial monomer concentration, moles/l.	Initial initiator concentration, moles/l.
M20A	20	0.18	3.996	0.0050
M20B	20	0.15	5.001	0.0077
M30A	30	0.77	2.985	0.0255
M30B	30	0.46	1.956	0.0159
M40A	40	0.50	0.9976	0.0099
M40B	40	0.33	1.495	0.0303

were taken to ensure that no air or water contaminated the reaction mixture. Scavenger levels of 0.15 to 0.77 millimoles of butyllithium per 100 g isoprene in the 100-cc reaction volume were obtained. (Scavenger level refers to the amount of butyllithium lost by adventitious impurities.) The scavenger levels are of the same order of magnitude as those reported by Hsieh.[3]

Isoprene conversions were determined by weighing the initial charge of isoprene and then by weighing the polymer produced. The polymer produced was precipitated by use of copious quantities of acetone. The polymer was dried by evaporating unreacted isoprene, benzene, and acetone in the hoods with subsequent drying in a vacuum oven. Cyanox SS, an antioxidant, was added to the polymer solution shortly after stopping the reaction. Butyllithium conversions were determined by terminating the reactions with water and analyzing the vapor phase by gas chromatography. Isobutane was injected into the mixture as a reference gas. This procedure has been reported by Hsieh.[3] Butyllithium conversions were also calculated by use of the number-average molecular weight determined by use of gel permeation chromatography and the grams of polymer produced. There was a considerable amount of scatter between the data of the two methods of analysis. The molecular weights and molecular weight distributions were determined by use of a gel permeation chromatograph. The procedure suggested by Aldhouse[4] was used to calculate molecular weights and molecular weight distributions. Additional details on the experimental procedure was reported by Porter.[5]

MODEL DEVELOPMENT

The polymerization of isoprene with n-butyllithium in benzene is a complex system of reactions. These reactions consist of association of butyllithium with itself and with poly(isoprenyllithium) as well as the association of poly(isoprenyllithium) with itself. However, the stoichiometry can be represented as
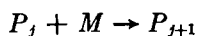Initiation

$$I + M \rightarrow P_1$$

TABLE II
Initiation Rate and Equilibrium Constants

Con-stant	Definition[a]	Values			Units
		20°C	30°C	40°C	
k_I	$(e^{19.51})e^{-6960/T}$	1.43×10^{-2}	3.14×10^{-2}	6.54×10^{-2}	l./(g-mole)(min)
K_1	$(e^{123.4})e^{-37,905/T}$	4.17×10^{-1}	2.98×10^1	1.62×10^3	(l./g-mole)^2
K_2	$(e^{-5.206})e^{3220/T}$	3.24×10^2	2.26×10^2	1.61×10^2	l./g-mole

[a] T is in degrees Kelvin.

Propagation

$$P_j + M \rightarrow P_{j+1}$$

The reactions are terminated by injection of an outside agent such as water.

Initiation Reaction

Because of the number of possible initiation reactions which may occur and of the low probability as indicated by Worsfold and Bywater[6] that the detailed mechanism can be delineated, an empirical rate equation was developed. This equation implies the existence of an association–dissociation mechanism with the addition of isoprene to an active form of butyllithium as being the rate-controlling step. The equation is

$$R_I = \frac{k_I I}{1 + K_1 I^2 + K_2 P_T} M = R_i' M. \tag{1}$$

The rate constants are presented in Table II. For low values of initial initiator concentration, the rate is first order with respect to butyllithium concentration. Similar results have been observed by Roovers and Bywater,[7,8] Hsieh,[9] Cramond,[10] and Porter et al.[11] for polymerization of isoprene in hydrocarbon solvents. The appearance of the term $(1 + K_1 I^2 + K_2 P_T)$ in the denominator indicates that high initial concentration of butyllithium retards the reaction. These terms probably represent association of the initiator with itself and of polymer with initiator. One notes the rate of initiation is first order with respect to the monomer, which agrees with results published by previous investigators. Numerous rate equations were tested, however, use of eq. (1) resulted in a minimum value for the sum of squares of deviation of the initiator conversions.

Propagation Reaction

Previous investigators have reported the rate of propagation as being first order with respect to the monomer and $^1/_4$ order with respect to the poly(isoprenyllithium). Numerous orders with respect to poly(isoprenyllithium) have been reported, however, the $^1/_4$ order seems to be accepted by several groups of investigators.[9,12] In the above-mentioned investigations, no initiator was present in the reaction mixture.

The $1/4$ order with respect to the poly(isoprenyllithium) was explained by an association–disassociation mechanism which has been extensively discussed by Porter, Ahmad, and Anthony.[11] The following reactions are assumed to exist:
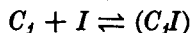
Rate controlling

$$C_j + M \xrightarrow{\ k_p\ } C_{j+1}$$
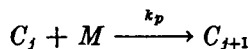
At equilibrium

$$4C_T \rightleftharpoons A_T; \quad K_p' = \frac{A_T}{C_T{}^4} \tag{2}$$

At equilibrium

$$C_j + I \rightleftharpoons (C_jI)$$

From these equations, Porter et al.[11] derived equations of the form

$$P_j = C_j(1 + 4K_p'C_T{}^3 + K_I I^a) \tag{3a}$$

and

$$P_T = C_T(1 + 4K_p'C_T{}^3 + K_I I^a) \tag{3b}$$

where C_T = concentration of total active polymer; P_T = concentration of total polymer; and C_j and P_j = concentration of active and total polymer of chain length j.

Given a set of constants and the total polymer concentration P_T, the value of C_T could be obtained. However, in this work the $4K_p'C_T{}^3$ was approximated by

$$4K_p'C_T{}^3 = (1 + K_p P_T{}^3)^{1/4}.$$

Substitution of this result into eq. (3) yields

$$P_j = C_j(1 + (1 + K_p P_T{}^3)^{1/4} + K_I I^a). \tag{4}$$

The rate of propagation then becomes

$$R_p = k_p C_T M = \frac{k_p P_T M}{1 + (1 + K_p P_T{}^3)^{1/4} + K_I I^2}. \tag{5}$$

Equation (5) has the property that if initiator concentration is zero and $K_p P_T{}^3 \gg 1$, then

$$R_p = \frac{k_p}{(K_p)^{1/4}} P_T{}^{1/4} M = k' P_T{}^{1/4} M. \tag{6}$$

This result is consistent with results obtained by other investigators. The values for k_p, K_p, and K_I are reported in Table III; a was found to be equal to 2. These constants were obtained by minimizing the sum of square of deviations of the isoprene conversion. This equation differs from that obtained in hexane solvent by Porter et al.[11] in that $(1 + K_p P_T{}^3)^{1/4} \cong 1 + 1/4 K_p P_T{}^3$ and the exponent a was $3/4$.

TABLE III
Propagation Rate and Equilibrium Constants

Con-stant	Definition[a]	Values			Units
		20°C	30°C	40°C	
k_p	$(e^{23.78})e^{-6320/T}$	0.912×10^1	1.86×10^1	3.62×10^1	l./(g-mole)(min)
K_p	$(e^{-41.38})e^{18600/T}$	3.97×10^9	4.89×10^8	6.87×10^7	(l./g-mole)^3
K_I	$(e^{-78.3})e^{14800/T}$	2.01×10^5	3.70×10^4	7.98×10^3	(l./g-mole)^2

[a] T is in degrees Kelvin.

Material Balance Equations and Distributions

The rate of formation of polymer specie of length j is obtained by

$$\frac{dP_j}{dt} = k_p M (C_{j-1} - C_j) \qquad 2 < j < \infty. \tag{7}$$

Substituting for C_j from eq. (3a) yields

$$\frac{dP_1}{d\tau} = R_i' - \alpha P_1 \tag{8a}$$

$$\frac{dP_j}{d\tau} = \alpha(P_{j-1} - P_j) \tag{8b}$$

where

$$\alpha = \frac{k_p}{1 + (1 + K_p P_T{}^3)^{1/4} + K_I I^2} \tag{9}$$

and

$$d\tau = M \, dt. \tag{10}$$

The moments of the distribution are as follows:

$$\lambda_0 = \Sigma P_j = P_T = I_0 X_I$$

$$\lambda_1 = \Sigma j P_j = M_0 X_m \text{ and } \lambda_2 = \Sigma j^2 P_j.$$

Multiplication of eqs. (8) by j^2 and summing over all j yields

$$\frac{d\lambda_2}{d\tau} = R_i' + \alpha(I_0 X_I) + 2\alpha(M_0 X_m). \tag{11}$$

The average degrees of polymerization are given by

$$\bar{D}_w = \lambda_2/M_0 X_m \tag{12}$$

$$\bar{D}_n = M_0 X_m/I_0 X_I. \tag{13}$$

Combining eq. (1) with a material balance on initiator and the definition of conversion yields

$$\frac{dX_I}{d\tau} = \frac{k_I(1 - X_I)}{1 + K_1 I_0{}^2(1 - X_I)^2 + K_2 I_0 X_I}. \tag{14}$$
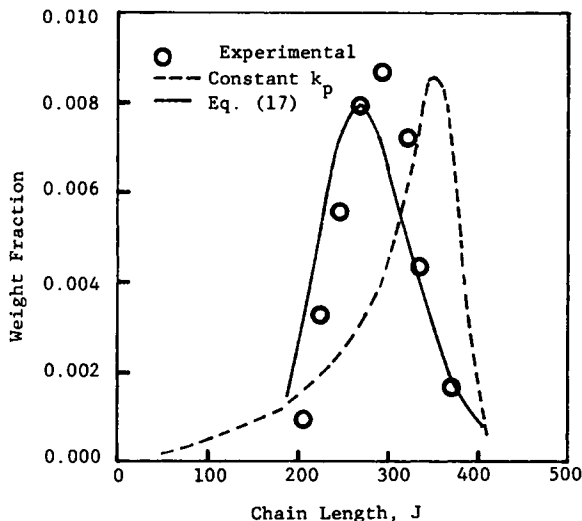
Fig. 1. Experimental and calculated molecular weight distributions, $r = 0.85$ for eq. (17) M20A5, $t = 60$ min.

Similarly, for the monomer,

$$M_0 \frac{dX_m}{d\tau} = I_0 \frac{dX_I}{d\tau} + \alpha[I_0 X_I]. \qquad (15)$$

Equations (11), (12), (13), (14), and (15) constitute the set of equations which must be solved in order to evaluate the average molecular weights and monomer and initiator conversions. Equations (11), (14), and (15) were integrated by use of Euler's method. The Hooke and Jeeves direct search procedure was used to obtain that set of constants which would minimize the sum of squares of deviation of initiator or monomer conversion. Real time was obtained by integrating

$$t = \int_0^\tau \frac{d\tau}{M(\tau)}$$

by use of the trapezoidal rule. The molecular weight distribution W_j as a function of j was calculated by use of the moment generating function method used by Liu and Amundson,[13] Edgar, Hasan, and Anthony,[14] Landon and Anthony,[15] and Porter et al.[11]

The calculated number-average molecular weight and isoprene and butyllithium conversions were in excellent agreement with the experimental data. However, the calculated weight-average molecular weight was 20–30% greater than the experimental values. Furthermore, the shape of the calculated molecular weight distribution curves were similar to the Gold[16] distributions, whereas the experimental curves are Gaussian in shape. This difference is illustrated in Figures 1 and 2. Porter et al.[11] obtained similar results for polymerization of isoprene in hexane. Therefore, the
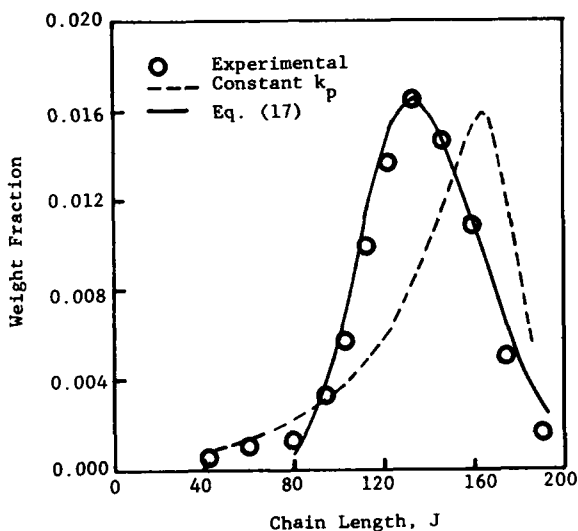
Fig. 2. Experimental and calculated molecular weight distributions M20B4, $t = 33$ min, $r = 0.97$ for eq. (17).

same procedure used by Porter et al.[11] which is similar to the use of variable k_p's as proposed by Mita[17] was utilized herein to obtain values of $\bar{D}_w$ that correlated with the experimental values. This procedure consisted of the use of a variable propagation constant as indicated in eqs. (16):

$$\frac{dP_1}{d\tau} = R_i' - \gamma\beta\, P_1 \tag{16a}$$

$$\frac{dP_j}{d\tau} = \gamma\beta(P_{j-1} - P_j) \qquad 2 \leqq j \leqq N \tag{16b}$$

and

$$\frac{dP_j}{d\tau} = \beta(P_{j-1} - P_j) \qquad j > N. \tag{16c}$$

The following equation was obtained for the second moment:

$$\frac{d\lambda_2}{d\tau} = R_i' + \alpha(I_0 X_I) + 2\alpha f_2(M_0 X_m) \tag{16d}$$

where

$$f_2 = \frac{1 + (\gamma - 1)f_1}{1 + (\gamma - 1)f_0}$$

and

$$f_0 = \sum_{j=1}^{N} P_j \Big/ \sum_{j=1}^{\infty} P_j$$

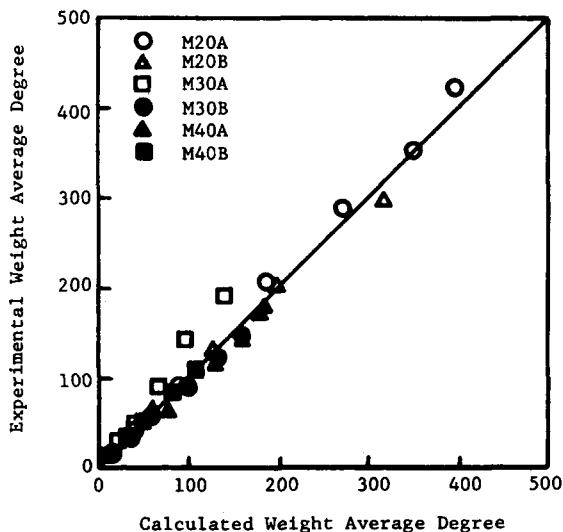$$f_1 = \sum_{j=1}^{N} jP_j \Big/ \sum_{j=1}^{\infty} jP_j$$

Fig. 3. Experimental and calculated weight average degrees of polymerization.

and

$$\beta = \frac{\alpha}{1 + (\gamma - 1)f_0}$$

where α is defined by eq. (9). The value of f_2 was obtained by minimizing the sum of squares of deviation of the weight average degree of polymerization. For four of the experimental runs, f_2 was between 0.88 and 0.92 with an average value of 0.90. For run M40A, a value of 0.8 was obtained for f_2. Calculated values of $\bar{D}_w$ using $f_2 = 0.9$ versus experimental values of $\bar{D}_w$ are shown in Figure 3. The use of an f_2 of 0.88 which was the weighted average for all five runs resulted in calculation of values for $\bar{D}_w$ less than $\bar{D}_n$.

The experimental MWD could be represented by a log normal distribution with correlation coefficients of 0.85 to 0.97. Therefore, instead of evaluating γ and N by use of the experimental distributions, the MWD may be calculated by use of the calculated average molecular weights; that is,

$$W_j = \frac{1}{\bar{D}_n \sigma \sqrt{2\pi}} \exp(-(\log_e j - \log_e \bar{J}_m)^2 / 2\sigma^2) \qquad (17)$$

$$\sigma^2 = \log \frac{\bar{D}_w}{\bar{D}_n}$$

$$\bar{J}_m = \sqrt{\bar{D}_w \cdot \bar{D}_n}.$$

DISCUSSION OF RESULTS

The experimental data are presented in Table IV. The isoprene conversion and initiator conversion versus time have the general character-

istics which have been reported for these systems. In Figures 4 and 5, monomer conversion and butyllithium conversion curves are presented for run M30B. Figures 6 and 7 illustrate the good agreement between calculated and experimental conversions.

TABLE-IV
Experimental Data

| Real time, min	Pseudo time, τ	X_I	X_M	$\bar{D}_n$	$\bar{D}_w$	$\bar{D}_w/\bar{D}_n$
		M20A, $M_0 = 3.996$, $I_0 = 0.0050$				
10	39.6	0.407	0.020	38	41	1.08
20	78.2	0.510	0.057	88	92	1.05
40	149.3	0.668	0.164	200	205	1.03
60	211.5	0.781	0.281	286	288	1.01
82	271.4	0.891	0.384	348	352	1.01
99	306.1	0.857	0.447	415	423	1.02
		M20B, $M_0 = 5.001$, $I_0 = 0.0077$				
18	88.4	0.430	0.042	60	65	1.08
33	157.6	0.604	0.116	124	131	1.06
50	229.0	0.745	0.211	197	203	1.03
82	342.4	0.845	0.373	289	293	1.01
		M30A, $M_0 = 2.985$, $I_0 = 0.0255$				
5	14.7	0.255	0.029	13	15	1.15
10	28.9	0.328	0.069	26	28	1.08
17	48.0	0.432	0.158	46	50	1.09
27	70.6	0.436	0.317	85	91	1.07
40	93.4	0.446	0.512	134	142	1.06
75	125.9	0.536	0.819	178	191	1.07
		M30B, $M_0 = 1.956$, $I_0 = 0.0159$				
5	9.7	0.222	0.027	14	15	1.07
13	24.4	0.390	0.094	31	34	1.10
22	39.3	0.466	0.216	57	61	1.07
35	58.0	0.552	0.395	87	93	1.07
50	72.9	0.621	0.596	118	124	1.05
75	87.3	0.679	0.784	142	148	1.04
		M40A, $M_0 = 0.9976$, $I_0 = 0.0099$				
10	9.0	0.366	0.222	57	61	1.07
20	15.1	0.478	0.554	109	115	1.06
30	18.3	0.518	0.771	140	146	1.04
51	21.0	0.531	0.937	167	173	1.04
80	21.6	0.545	1.000	173	181	1.05
		M40B, $M_0 = 1.495$, $I_0 = 0.0303$				
8	9.9	0.201	0.121	30	33	1.10
15	18.0	0.320	0.348	54	58	1.07
25	25.3	0.413	0.658	78	84	1.08
40	30.4	0.553	0.849	76	82	1.08
60	33.0	0.463	0.953	101	106	1.05
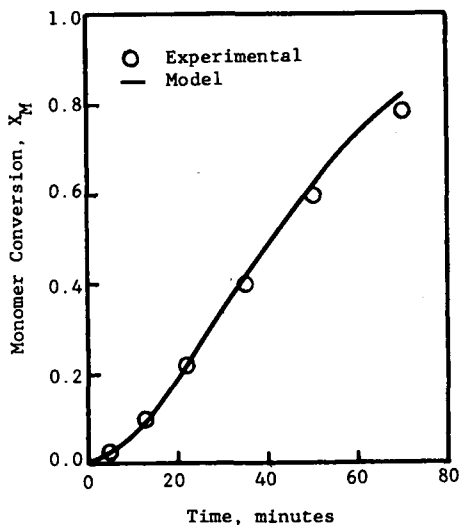
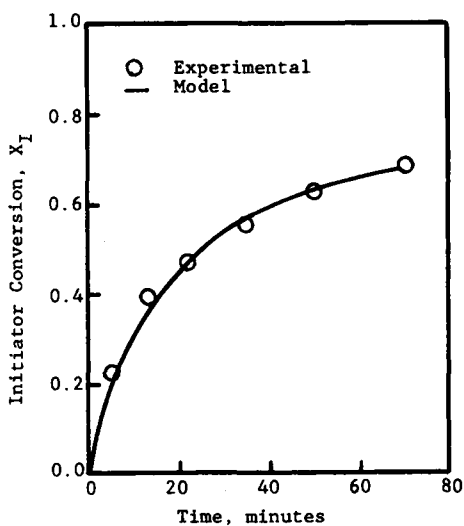Fig. 4. Isoprene conversion, run M30B.

Fig. 5. Butyllithium conversion, run M30B.

Figures 3 and 8 illustrate the excellent agreement obtained between calculated and experimental weight-average and number-average molecular weights.

The fact that the experimental distributions could be represented with a log normal distribution even though initiation was continuous throughout the reaction illustrates the importance of the association reactions or of a variable k_p in obtaining a narrow distribution. The failure of eq. (8) to account for this effect suggests an improper formulation of the association of polymer with initiator, nonvalidity of the rate-controlling assumption, improper weighting of the association equilibrium constants, or, as implied
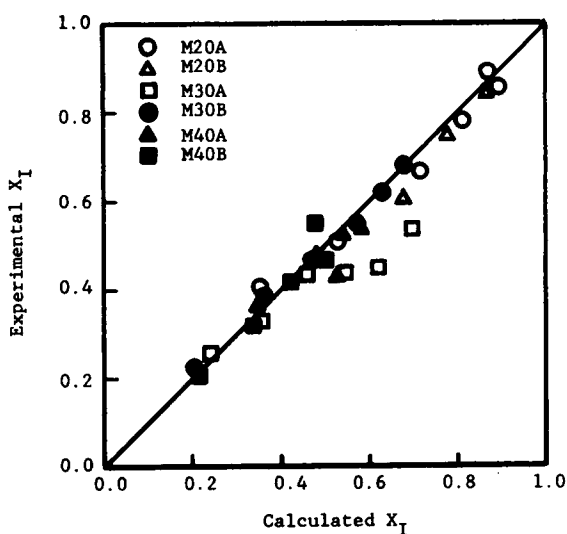
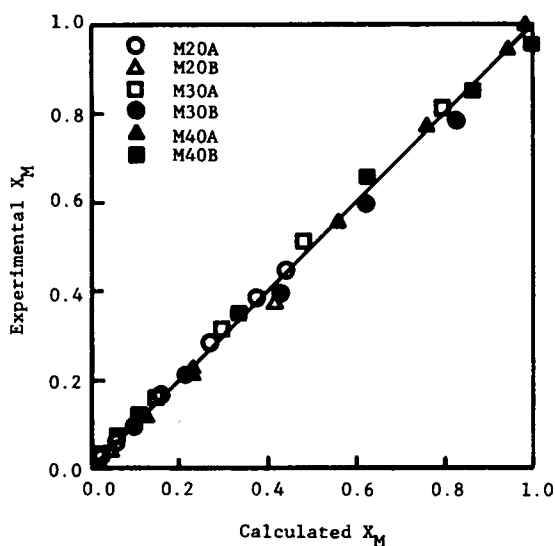Fig. 6. Experimental and calculated butyllithium conversion.

Fig. 7. Experimental and calculated isoprene conversion.

by eqs. (16), that the smaller chains propagate faster than the longer polymer chains. In any event, the use of a variable propagation constant as was done in eqs. (16) yields a satisfactory estimate of the weight-average degree of polymerization.

CONCLUSIONS

A mathematical model has been developed for the batch polymerization of isoprene in benzene for concentrations of 1 to 5 molar and initiator con-
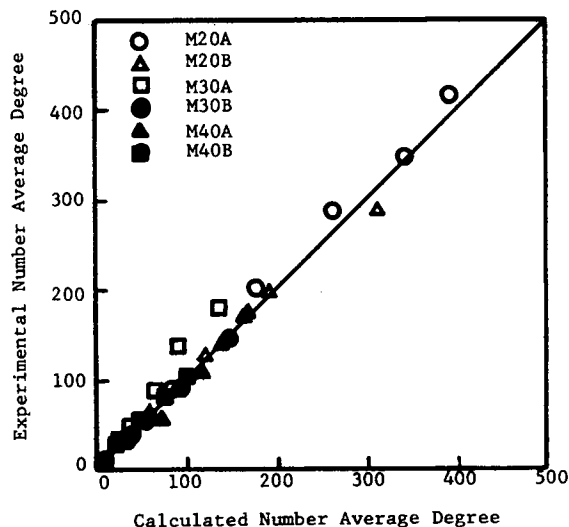
Fig. 8. Experimental and calculated number-average degrees of polymerization.

centrations of 0.005 to 0.03 molar. The rate equations for propagation and initiation can readily be used in the material balances for flow reactors. The values of γ, N, and β should remain the same while those of f_0 and f_1 should definitely change. The value of f_2 may remain constant since it is a ratio. The resulting distribution would, however, probably be skewed.

Nomenclature

I, M	concentration of butyllithium and isoprene, when used in material balance or rate equations
P_j	polymer of length j
C_j	active polymer of length j
I_0, M_0	initial concentrations
$\bar{D}_n$, $\bar{D}_w$	number- and weight-average degree of polymerization
X_I, X_m	initiator and monomer conversions
P_T	ΣP_j = total polymer
C_T	ΣC_j = total active polymer
A_T	total associated polymer
r	correlation coefficient

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