

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

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Synopsis

Isoprene was polymerized in batch reactors by use of bottle polymerization techniques at 30°, 40°, and 50°C at concentrations from 1 to 5 molar. Butyllithium concentration was varied from 0.005 to 0.03 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 hexane 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 a *cis*-1,4 polyisoprene similar to *heva* natural rubber is produced.

EXPERIMENTAL

Seven runs consisting of 40 samples were conducted in batch reactors at 30°, 40°, and 50°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. Baker instra-analyzed hexane 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 hexane. This solution was diluted in hexane 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 Harris¹ and Uranek et al.² The polymerization bottles were dried and rinsed with butyllithium solution and rerinsed with purified hexane before use. Numerous precautions were taken to insure that no air or water con-

TABLE I
 Initial Conditions

Run no.	Temp., °C	Scavenger level, mmoles BuLi/100 g	Initial monomer concn., moles/l.	Initial initiator concn., moles/l.
P30A	30	0.55	1.24	0.0311
P30B	30	0.55	5.00	0.00727
P40A	40	0.55	1.99	0.0154
A40A*	40	0.55	1.99	0.0159
P40B	40	0.55	3.06	0.00993
P50A	50	0.55	0.988	0.0209
P50B	50	0.55	3.94	0.00533

* This run was made by starting with practical-grade mixed hexanes and practical-grade isopropene, and purifying the reagents by the same procedures used in the P-experiments which were conducted at an earlier date.

taminated the reaction mixture. Scavenger levels of 0.2 to 0.8 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 average value used in this work was 0.55 millimoles per 100 g monomer. 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, hexane, and acetone in the hoods with subsequent drying in a vacuum oven. Cynox 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. In general, the two conversions thus calculated were in good agreement. The molecular weights and molecular weight distributions were determined by use of a gel permeation chromatograph. The procedure suggested by Aldhouse⁴ was used to calculate molecular weights and molecular weight distributions. Additional details on the experimental procedure are reported by Porter⁵ and Ahmad.⁶

MODEL DEVELOPMENT

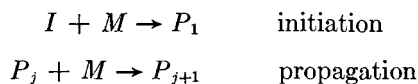
The polymerization of isoprene with *n*-butyllithium in hexane is a complex system of reactions. These reactions consist of association of butyllithium with itself and with poly(isoprenyllithium) as well as the association

TABLE II
Initiation Rate and Equilibrium Constants^a

Constant	Definition	Values			Units
		30°C	40°C	50°C	
k_a	$4.39 \times 10^7 e^{-6930/T}$	0.00514	0.0107	0.0212	1./[(g-mole) (min)]
k_b	$1.14 \times 10^{23} e^{-16700/T}$	0.133	0.775	4.04	[(l./g-mole)] ² (min) ⁻¹
K_1	$6.58 \times 10^5 e^{-1340/T}$	7,920	9,130	10,400	[l./g-mole] ²
ϕ	$2.60 \times 10^{15} e^{-9770/T}$	25.9	72.7	191.	l./g-mole

^a T is in degrees Kelvin; $\phi = k_b/k_a$.

of poly(isoprenyllithium) with itself. However, the stoichiometry can be represented as



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 Bywater⁷ 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

$$R_I = \frac{k_a I + k_b I P_T}{1 + K_1 I^2} M. \quad (1)$$

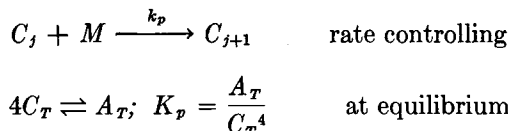
The rate constants are presented in Table II. For low values of initial initiator concentration, the rate is first order with respect to butyllithium concentration. Roovers and Bywater^{8,9} have observed similar results in the study of the isoprene-butyllithium-hexane system. The appearance of the $K_1 I^2$ term in the denominator indicated that high initial concentration of butyllithium retards the reaction. This term probably represents association of the initiator with itself. A similar term for association of poly(isoprenyllithium) with initiator may exist; however, our data did not warrant inclusion of this term in the rate equation. 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.^{10,11} 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 illustrated as follows:



and

$$P_T = C_T + 4A_T = C_T + 4K_p C_T^4 \cong 4K_p C_T^4 \quad (2)$$

therefore

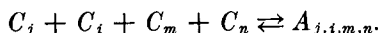
$$C_T = (P_T/4K_p)^{1/4}$$

and

$$R_p = k_p C_T M = \frac{k_p}{(4K_p)^{1/4}} P_T^{1/4} M \quad (3)$$

$$= k' P_T^{1/4} M. \quad (4)$$

The association reaction could be represented in more detail as



With this detail, the total polymer of length j which can be measured is

$$P_j = C_j + 4A_{4j} + \sum_{i \neq j} (3A_{3j,i} + A_{3i,j}) + 2 \sum_{i \neq j} A_{2j,2i} + \sum_{i \neq j} \sum_{n \neq i} A_{2j,i,n} \\ + \sum_{i \neq m \neq n \neq j} \sum \sum A_{j,i,m,n} \quad (5)$$

where $n > m > i \neq j$.

Therefore, summing over all j ,

$$P_T = C_T + 4A_T \quad (6)$$

where

$$A_T = \frac{1}{4} \sum_{j=1}^{\infty} \left\{ 4A_{4j} + \sum_{i \neq j} (3A_{3j,i} + A_{3i,j} + 2A_{2j,2i}) \right. \\ \left. + \sum_{i \neq j} \sum_{n \neq i} A_{2j,i,n} + \sum_{i \neq m \neq n \neq j} \sum \sum A_{j,i,m,n} \right\}. \quad (7)$$

where $n > m > i$.

If $A_{j,i,t,m,n} = K_{j,i,t,m,n}$, $C_j C_i C_m C_n$ is substituted into eq. (7), and the result is compared with $A_T = K_p C_T^4$, then

$$\begin{aligned} K_{4j} &= K_p \\ K_{3j,t} &= 4K_p \quad i \neq j \\ K_{2j,2t} &= 12K_p \quad i \neq j \\ K_{2j,i,m} &= 24K_p \quad i \neq j \neq m \\ K_{i,j,m,n} &= 96K_p \quad i \neq j \neq m \neq n. \end{aligned} \quad (8)$$

Equation (8) shows a greater probability of finding an associated polymer molecule composed of lithium-polymer chains of different lengths than of finding any of the other possible combinations.

For the polymer species of length j and the equalities given by eq. (8),

$$P_j = C_j (1 + 4K_p C_T^3). \quad (9)$$

Summation of eq. (9) over all j yields eq. (2).

In our study, both initiation and propagation were occurring simultaneously, therefore, an additional association of polymer with initiator must be considered. The reaction considered was



with

$$[C_j I] = K_2 C_j I^a \quad (10b)$$

The a is added to account for the possibility of association of the butyllithium. Addition of eq. (10b) to eq. (9) yields

$$P_j = C_j (1 + 4K_p C_T^3 + K_2 I^a). \quad (11)$$

Summing over all j ,

$$P_T = C_T (1 + 4K_p C_T^3 + K_2 I^a). \quad (12)$$

For any set of $\{K_p, K_2, \text{ and } P_T\}$, eq. (12) may be solved by Newton's method to obtain a value for C_T to substitute into eq. (3). However, eq. (12) is similar in form to results obtained by Landon and Anthony¹² in a study of the polymerization of styrene. Therefore, the active polymer concentration was approximated by an equation of the form

$$C_j = P_j / (1 + K_2 I^a + K_3 P_T^b) \quad (13a)$$

$$C_T = \frac{P_T}{1 + K_2 I^a + K_3 P_T^b} \quad (13b)$$

The use of this form for C_T eliminates the trial-and-error procedure required by eq. (12). The values of a and b were found to be equal to $3/4$ and 3. Since it was desired to have C_T proportional to $P_T^{1/4}$ in the limit as initiator concentration approached zero, a value of $b = 3/4$ was considered.

TABLE III
 Propagation Rate and Equilibrium Constants

Constant	Definition ^a	Values			Units
		30°C	40°C	50°C	
k_p	$2.68 \times 10^6 e^{-3140/T}$	8.47	11.8	16.1	l./[(g-mole) (min)]
K_2	$1.03 \times 10^{-11} e^{9180/T}$	148.	56.2	22.7	[l./g-mole] ^{3/4}
K_3	$4.08 \times 10^{-2} e^{6660/T}$	5.28×10^6	2.91×10^6	1.66×10^6	[l./g-mole] ³

^a T is in degrees Kelvin.

However, the value of $b = 3$ gave the minimum value for the sum of squares based on the isoprene conversion. The values of the constants are presented in Table III. Examination of the order of magnitude of $K_3 P_T^3$ shows that only in the later stages of the polymerization does polymer association become important. That is, over most of the range studied, the association of polymer with initiator controls the active polymer concentration. Hence, $b = 3$ might be justified by considering the term $(1 + 4K_3 P_T^3)^{1/4} = 1 + K_3 P_T^3$ if $4K_3 P_T^3 < 1$. This approximation begins to fail only at high initiator conversion and was, therefore, valid over most of the range of concentrations considered.

In view of these results, eq. (12) was solved for C_T by Newton's method, and the sum of squares was approximately equal to that obtained by use of eq. (13) for C_T . Also, only the ratios of (k_p/K_p) , (K_2/K_p) , or (k_p/K_2) could be obtained. The association with initiator was most important initially, with polymer association becoming important at the high initiator conversions. Since eq. (13) does not require the added trial-and-error calculations, it was used in the subsequent calculations.

MATERIAL BALANCE EQUATIONS AND DISTRIBUTIONS

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

$$\frac{dP_j}{dt} = k_p M (C_{j-1} - C_j) \quad 2 < j \leq \infty. \quad (14)$$

Substituting for C_j from eq. (13a) yields

$$\frac{dP_1}{d\tau} = R_i' + \alpha P_1 \quad (15a)$$

$$\frac{dP_j}{d\tau} = \alpha (P_{j-1} - P_j) \quad (15b)$$

where

$$\alpha = \frac{k_p}{1 + K_2 I^{3/4} + K_3 P_T^3} \quad (16)$$

and

$$d\tau = M dt. \quad (17)$$

The moments of the distribution are as follows:

$$\begin{aligned}\lambda_0 &= \sum P_j = P_T = I_0 X_I \\ \lambda_1 &= \sum j P_j = M_0 X_m \text{ and } \lambda_2 = \sum j^2 P_j.\end{aligned}$$

Multiplication of eqs. (15) by j^2 and summing over all j yields

$$\frac{d\lambda_2}{d\tau} = R_i' + \alpha(I_0 X_I) + 2\alpha(M_0 X_m). \quad (18)$$

The average degrees of polymerization are given by

$$\bar{D}_w = \lambda_2 / M_0 X_m \quad (19)$$

$$\bar{D}_n = M_0 X_m / I_0 X_I. \quad (20)$$

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

$$\frac{dX_I}{d\tau} = \frac{k_a(1 - X_I)(1 + \phi(I_0 X_I))}{1 + K_1 I_0^2 (1 - X_I)^2}. \quad (21)$$

Similarly, for the monomer,

$$M_0 \frac{dX_m}{d\tau} = I_0 \frac{dX_I}{d\tau} + \alpha[I_0 X_I]. \quad (22)$$

Equations (18), (19), (20), (21), and (22) constitute the set of equations which must be solved in order to evaluate the average molecular weights and monomer and initiator conversions. Equations (18), (21), and (22) 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 and Landon and Anthony.¹²

The calculated number-average molecular weight and isoprene and butyllithium conversions were in excellent agreement with the experimental data. However, the calculated weight-average degree of polymerization was 25–35% greater than the experimental values. Furthermore, the shape of the calculated molecular weight distribution curves were similar to the Gold¹⁵ distributions, whereas the experimental curves were Gaussian in shape. This difference is illustrated in Figure 1. The same result was obtained by use of eqs. (11) and (12) to calculate the active polymer concentration.

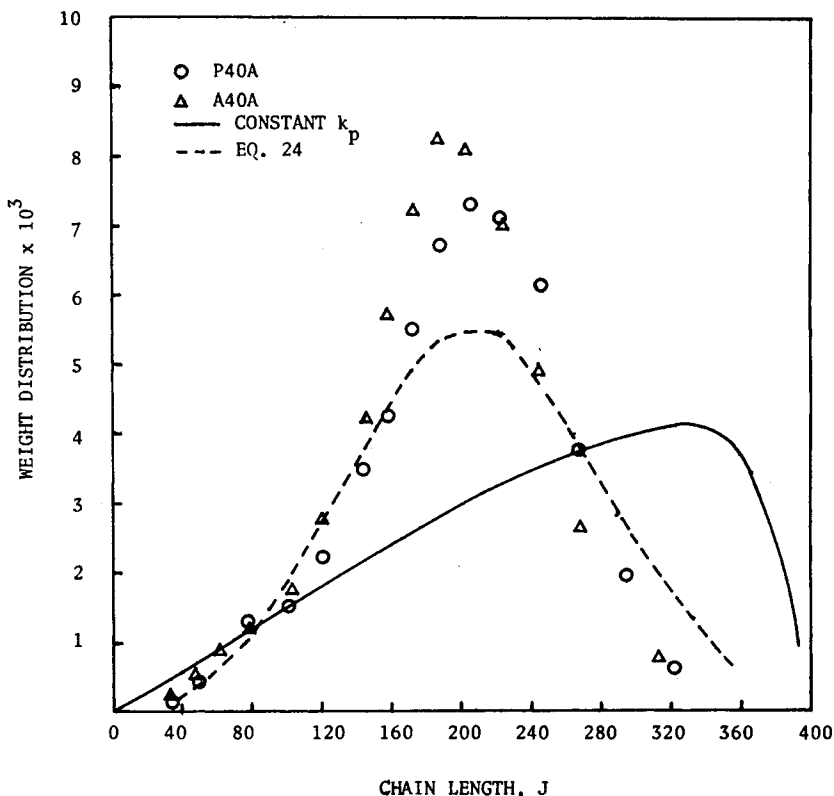


Fig. 1. Typical molecular weight distribution—A40A; $t = 70$ min.

Examination of Figure 1 shows a need for the model to have a lower concentration of short and long chains and a higher concentration of intermediate chains. The use of a variable propagation constant as indicated in eqs. (23) was considered:

$$\frac{dP_1}{d\tau} = R_i' + \gamma\beta P_1 \quad (23a)$$

$$\frac{dP_j}{d\tau} = \gamma\beta(P_{j-1} - P_j) \quad 2 \leq j \leq N \quad (23b)$$

and

$$\frac{dP_j}{d\tau} = \beta(P_{j-1} - P_j) \quad j > N. \quad (23c)$$

The following equation was obtained for the second moment:

$$\frac{d\lambda_2}{d\tau} = R_i' + \alpha(I_0 X_I) + 2\alpha f_2 (M_0 X_m) \quad (23d)$$

where

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

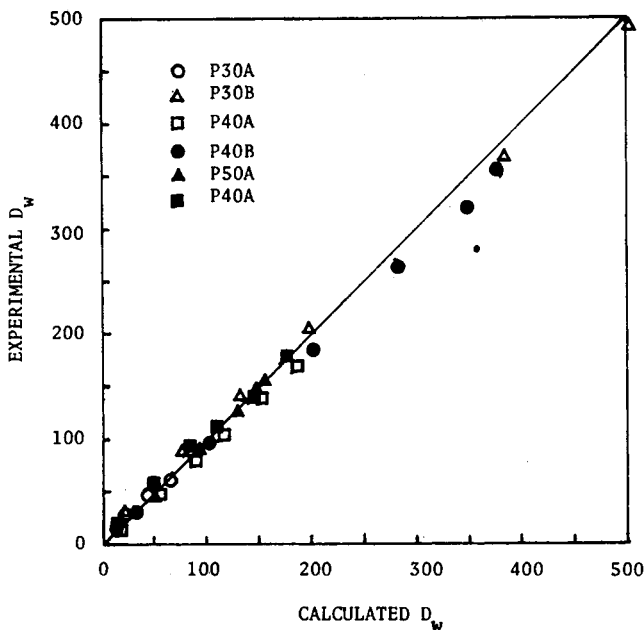


Fig. 2. Comparison of experimental and calculated weight-average degrees of polymerization.

and

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

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

and

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

where α is defined by eq. (16). The value of f_2 was obtained by minimizing the sum of squares of the weight-average degree of polymerization. For the seven experimental runs, f_2 was between 0.82 to 0.87 with an average value of 0.85. Calculated values of \bar{D}_w using $f_2 = 0.85$ versus experimental values of \bar{D}_w are shown in Figure 2.

The experimental MWD could be represented by a normal distribution with a correlation coefficient of 0.94 or better. 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,

$$W_j = \frac{j}{\bar{D}_n \sigma \sqrt{2\pi}} \exp \left\{ - (j - \bar{D}_n)^2 / 2\sigma^2 \right\} \quad (24)$$

where

$$\sigma^2 = (\bar{D}_w - \bar{D}_n) \bar{D}_n.$$

DISCUSSION OF RESULTS

The experimental data are presented in Table IV. The data for run P50B were not used in the development of the model as we suspected the reaction was nonisothermal. The microstructure of six samples was analyzed by use of the procedure described by Silas, Yates, and Thornton.¹⁶ The cis contents were found to be $65\% \pm 1\%$, with 3,4-addition of approximately 6.5%. These cis contents are typical for low molecular weight polymer made with butyllithium.¹⁷ The isoprene conversions and initiator conversions versus time have the general characteristics which have been reported for these systems. In Figures 3 and 4, monomer conversion and butyllithium conversion curves are presented for run P30B. Figures 5 and 6 illustrate the good agreement between calculated and experimental conversions. In some cases, a higher initiator conversion was obtained by use of the gas-chromatographic analysis than that obtained by calculating initiator conversion from molecular weight data. For these cases, butane probably leaked from the bottles, therefore, the conversions obtained by GPC were utilized in the development of the rate equation for initiation. The value of k_a obtained in eq. (1) at 50°C is approximately equal to the initiation rate constant presented by Hsieh.¹⁷

Figures 2 and 7 illustrate the excellent agreement obtained between calculated and experimental weight-average and number-average molecular weights. Shown in Figure 8 is a comparison of data reported by Hsieh,¹⁷ our experimental data, and the values calculated by the model.

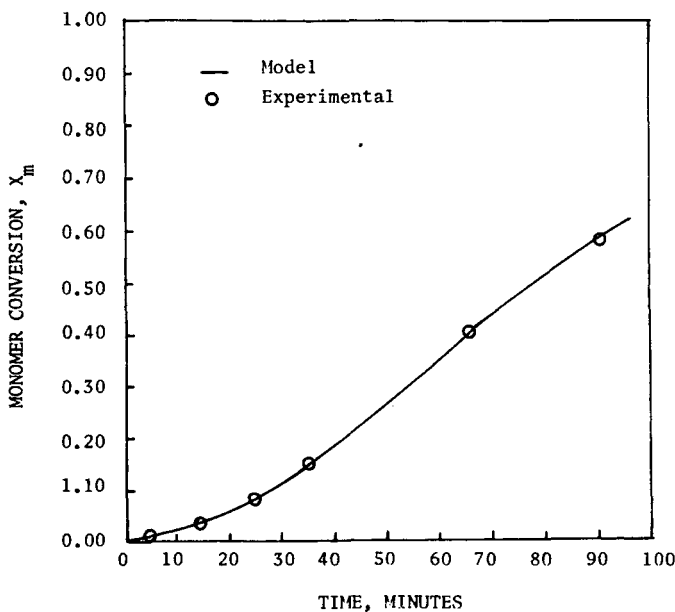


Fig. 3. Variation of isoprene conversion for Run P30B.

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
--- P30A, $M_0 = 1.24, I_0 = 0.031$						
30	36	0.020	0.031	14	18	1.31
60	72	0.056	0.050	29	35	1.23
100	119	0.079	0.093	46	53	1.18
150	173	0.114	0.176	61	70	1.18
--- P30B, $M_0 = 5, I_0 = 0.0073$						
5	25	0.069	0.007	24	29	1.19
15	74	0.250	0.031	87	97	1.16
20	121	0.401	0.082	141	155	1.13
35	165	0.521	0.155	204	220	1.12
65	272	0.670	0.401	368	389	1.10
90	336	0.743	0.578	466	486	1.09
--- P40A, $M_0 = 1.99, I_0 = 0.0154$						
5	10	0.059	0.018	14	18	1.35
15	29	0.119	0.044	48	56	1.19
25	47	0.167	0.099	77	88	1.18
35	65	0.228	0.182	103	118	1.17
50	87	0.313	0.338	140	156	1.15
70	109	0.421	0.550	169	189	1.15
--- P40B, $M_0 = 3.06, I_0 = 0.0099$						
5	15	0.078	0.015	33	39	1.21
15	44	0.256	0.081	97	109	1.15
30	82	0.502	0.299	184	202	1.14
50	115	0.709	0.602	262	286	1.13
80	139	0.769	0.852	319	353	1.14
150	152	0.823	0.983	356	384	1.12
--- P50A, $M_0 = 0.988, I_0 = 0.0209$						
5	4.9	0.022	0.038	16	20	1.26
15	14.3	0.084	0.083	47	54	1.20
30	26.6	0.133	0.244	86	99	1.18
50	38.6	0.202	0.542	127	144	1.17
70	45.3	0.251	0.758	143	162	1.17
90	48.5	0.280	0.907	153	171	1.15
--- P50B, $M_0 = 3.94, I_0 = 0.0053$						
2	7.9	0.153	0.015	68	77	1.17
4	15.6	0.234	0.036	149	166	1.14
8	29.4	0.602	0.259	338	364	1.13
13	40.4	0.608	0.588	607	629	1.10
18	46.5	0.767	0.780	614	631	1.10
22 ¹ / ₄	49.1	0.560	0.882	933	969	1.11
--- A40A, $M_0 = 1.99, I_4 = 0.0159$						
5	9.9	0.053	0.018	21	25	1.19
15	29.1	0.108	0.05	57	66	1.16
25	47.4	0.163	0.116	87	104	1.18
35	64.0	0.229	0.210	112	131	1.16
50	85.4	0.334	0.382	140	168	1.19
70	105.8	0.418	0.599	176	202	1.15

The fact that the experimental distributions were Gaussian 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. (15) or, more specifically, eqs. (12) and

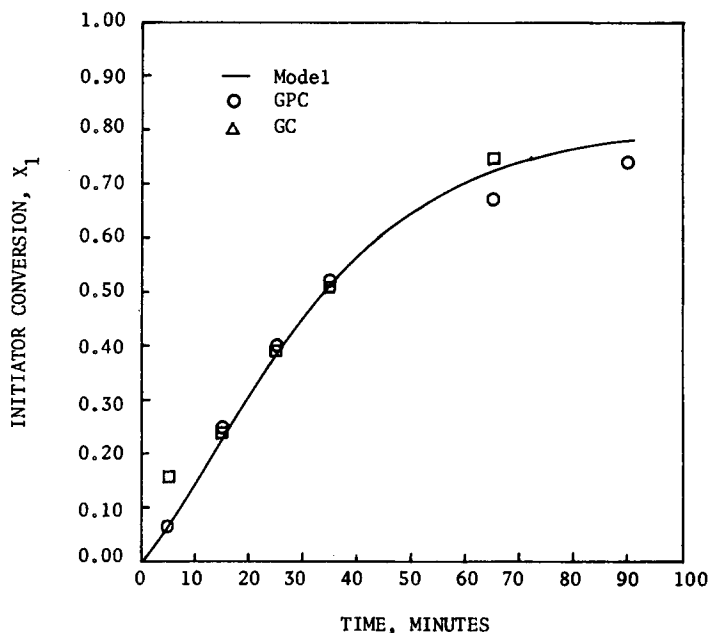


Fig. 4. Initiator conversion by GPC and GC for Run P30B.

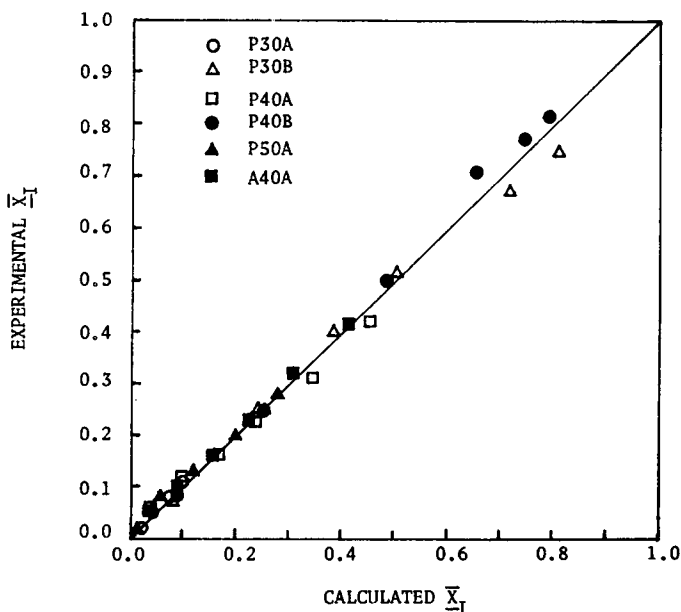


Fig. 5. Comparison of experimental and calculated butyllithium conversions.

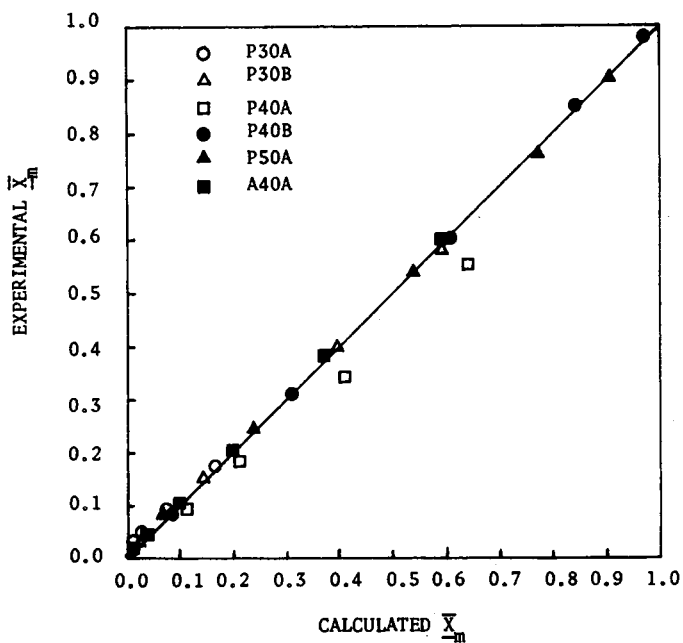


Fig. 6. Comparison of experimental and calculated isoprene conversions.

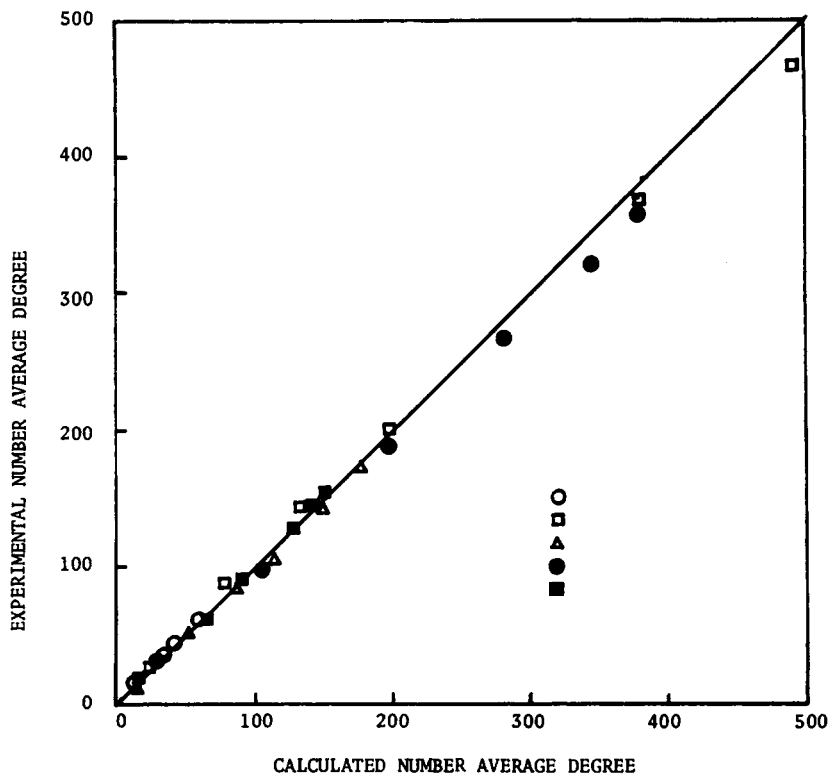


Fig. 7. Deviation of calculated to experimental number-average degree of polymerization: \circ P30A; \square P30B; \triangle P40A; \bullet P40B; \blacksquare P50A.

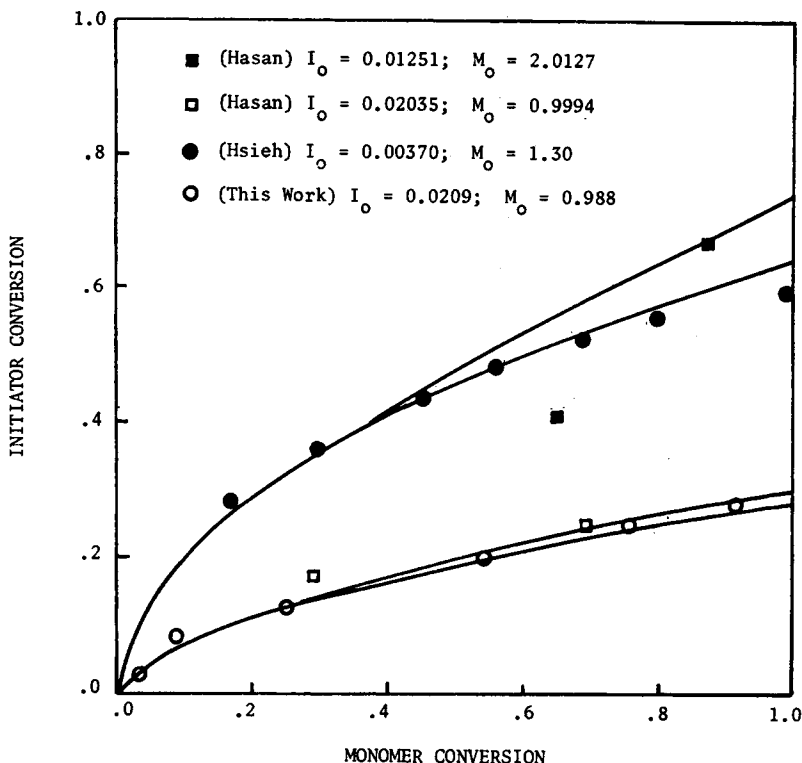
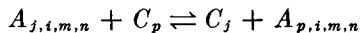
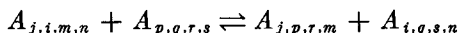


Fig. 8. Other investigators' work at 50°C.

(13) 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 by eqs. (23), the smaller chains propagate faster than the longer polymer chains. The latter case would probably be caused by steric hindrance through coiling of the longer polymer chains. Nonvalidity of the rate-controlling assumption would be due to the failure to establish the equilibrium composition between the small associated molecules and the longer chains as the reaction proceeds. This reaction may be represented as



or



where $i,j,m,n > p,q,r,s$. While a general equilibrium of total active to total associated may be satisfied, equilibrium as indicated by these reactions may not be well established. In any event, the use of a variable propagation constant as was done in eq. (23) yields a satisfactory estimate of the weight-average degree of polymerization.

CONCLUSIONS

A mathematical model has been developed for the batch polymerization of isoprene for concentrations of 1 to 5 molar and initiator concentrations 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
$A_{j,i,m,n}$	associated polymer composed of lithium polymer chains of length j, i, m, n
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	$\sum P_j =$ total polymer
C_T	$\sum C_j =$ total active polymer
A_T	total associated polymer

The support of the Texas Engineering Experiment Station and National Science Foundation is greatly appreciated. The analysis of the cis-trans content of the polymer was done by Phillips Petroleum Company, Bartlesville, Oklahoma.

References

1. J. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).
2. C. A. Uraneck, J. E. Burleigh, and J. W. Cleary, *Anal. Chem.*, **40**, 327 (1968).
3. H. L. Hsieh, *J. Polym. Sci. A*, **3**, 153 (1965).
4. S. T. E. Aldhouse and D. M. Standford, *Proceedings Fifth International Seminar Gel Permeation Chromatography*, London, 1968.
5. R. E. Porter, M.S. Thesis, Texas A&M University, Texas, 1972.
6. A. Ahmad, Master of Engineering Report, Texas A&M University, Texas, 1972.
7. D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **42**, 2884 (1964).
8. J. E. L. Roovers and S. Bywater, *Faraday Soc. Trans.*, **62**, 701 (1966).
9. J. E. L. Roovers and S. Bywater, *Macromolecules*, **1**, 328 (1968).
10. H. Hsieh and W. H. Glaze, *Rubber Chem. Technol.*, **43**, 22 (1970).
11. M. Morton, R. A. Pett, and L. J. Fetters, *Preprint 2.1.10, IUPAC Macromolecular Symposium*, Tokyo, Japan, 1966.
12. J. R. Landon and R. G. Anthony, *A.I.Ch.E.J.*, **18**, 843 (1972).
13. S. N. Liu and N. R. Admundson, *Chem. Eng. Sci.*, **17**, 797 (1962).
14. T. D. Edgar, S. Hasan, and R. G. Anthony, *Chem. Eng. Sci.*, **25**, 1463 (1970).
15. L. Gold, *J. Chem. Phys.*, **28**, 1, 91 (1958).
16. R. S. Silas, J. Yates, and V. Thornton, *Anal. Chem.*, **31**, 529 (1959).
17. H. L. Hsieh, *J. Polym. Sci.*, **A3**, 181 (1965); personal communication, Dec. 18, 1972.

Received October 24, 1973