R & D NOTES

A Mathematical Model for Polymerization of Styrene with *n*—Butyllithium in Cyclohexane

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In the design, optimization, and control of polymerization reactors, it is desirable to have a mathematical model which can be used to estimate molecular weight distributions (MWD) and monomer and initiator conversions for a given set of reactor conditions. While many theoretical models have been proposed in the literature, a limited amount of work has been presented which supports the proposed models with experimental data. The objective, therefore, of this study was to obtain data which could be used in evaluating the kinetic parameters in a model for predicting MWD and monomer and initiator conversions in the styrene-butyllithium-cyclohexane system. These new data should also add to the understanding of this polymerization system.

Styrene conversions, molecular weights, and molecular weight distributions were measured as a function of time in batch reactors. Butyllithium conversions were calculated as follows:

$$X_I = \frac{M_0 X_m}{I_0 \overline{D}_n}$$

These data are presented in Table 1. Bottle polymerization techniques were utilized and the MWD's were determined by use of Gel Permeation Chromatography.[*] An empirical relation was developed to correct for the effect of dispersion on the average molecular weights. Detailed experimental procedures are presented by Landon (1971).

The initiation reactions in this system are very complex; therefore, by use of nonlinear regression the following equation was developed:

$$R_I' = I_0 \frac{dX_I}{d\tau} = k_1 I^{1/6} + k_2 I_0{}^{-2.35} M_0{}^{1.8} I^{2.25} P_T{}^{1.6}$$

$$k_1 = 1.093 \times 10^4 \exp\left[\frac{-5577}{T}\right]; \qquad \left(\frac{L}{m}\right)^{1/6} \frac{1}{\text{min}}$$

$$k_2 = 0.63 \times 10^{19} \exp\left[\frac{-13195}{T}\right]; \qquad \left(\frac{L}{m}\right)^{3.3} \frac{1}{\text{min}}$$

By following the procedures presented by Edgar et al. (1970) the following equations for calculating the monomer conversions, molecular weights, and molecular weight distributions can be derived for an association-disassociation mechanism:

$$M_0 \frac{dX_m}{d\tau} = R_I' + \alpha P_T$$

$$\alpha = \frac{k_p}{1/2 + \sqrt{1/4 + 2K_P{}^{-1} P_T}}, \qquad P_T = I_0 X_I$$

$$D_n = \frac{M_0 X_m}{I_0 X_I}$$

$$D_w = 1 + \frac{2\int_0^\tau \left\{ R_I' \int_{\tau_1}^\tau \alpha d\tau_2 \right\} d\tau_1 + \int_0^\tau R_I' \left\{ \int_{\tau_1}^\tau \alpha d\tau_2 \right\}^2 d\tau_1}{M_0 - M}$$

$$W_j = \frac{jP_j}{M_0 - M}$$

$$= \frac{j}{M_0 - M} \left\{ \int_0^\tau \left\{ R_I' \exp\left[- \int_{\tau_1}^\tau \alpha d\tau_2 \right] \frac{1}{(j-1)!} \left[\int_{\tau_1}^\tau \alpha d\tau_2 \right]^{j-1} \right\} d\tau_1 \right\}$$

The numerical methods which were used to evaluate the differential equations were the Runge-Kutta and Eulers procedure. The integrals were evaluated by Simpson's and the trapezoidal rule. After an equation for the initiation reactions was obtained, the grouped propagation constant k' and the values of k_P and K_P were evaluated by minimizing the sum of the squares of deviation on styrene conversion plus the square of % deviation of the weight average molecular weight. The values of k_p, k', and K_p are reported in Table 2.

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[*] GPC data as a function of time are on permanent files, Department of Chemical Engineering, Texas A&M University.

TABLE 1. EXPERIMENTAL DATA

Run number	Real time, min	Monomer conversion	Initiator conversion	Tau	*Dn*	*Dw*	*Dw/Dn*
I A	10	0.087	0.145	9.6	120	153	1.28
I A	20	0.187	0.179	18.2	209	307	1.47
I A	30	0.285	0.246	25.6	231	360	1.56
I A	40	0.429	0.299	32.3	287	419	1.46
I A	50	0.552	0.388	37.6	284	429	1.51
I A	60	0.664	0.564	41.5	235	410	1.74
I A	70	0.738	0.544	44.5	271	480	1.77
I A	73	0.766	0.635	45.2	241	432	1.79
I A	90	0.877	0.592	48.3	296	454	1.53
I A	110	0.935	0.579	50.1	323	466	1.45
I A	240	0.995	0.672		298	485	1.63
I B	10	0.090	0.069	9.6	131	168	1.29
I B	20	0.196	0.112	18.2	175	245	1.40
I B	30	0.294	0.163	25.6	180	293	1.63
I B	30	0.319	0.150	25.6	213	300	1.41
I B	40	0.493	0.203	31.6	243	347	1.43
I B	50	0.618	0.281	36.3	220	347	1.58
I B	50	0.576	0.251	36.3	228	355	1.56
I B	60	0.686	0.245	39.8	280	379	1.36
I B	70	0.771	0.294	42.5	263	382	1.46
I B	87.25	0.875	0.294	45.6	298	406	1.37
I B	110	0.952					
II A	5	0.055	0.077	4.88	143	200	1.41
II A	10	0.205	0.218	9.28	188	306	1.62
II A	20	0.559	0.446	15.35	250	376	1.50
II A	35	0.837	0.624	19.46	268	425	1.58
II A	80	0.980	0.673	22.20	291	454	1.56
II B	5	0.093	0.072	4.77	127	178	1.39
II B	5	0.091	0.050	4.77	185	291	1.58
II B	10	0.264	0.154	8.87	171	235	1.34
II B	15	0.426	0.213	12.05	200	293	1.47
II B	20	0.647	0.284	14.24	228	388	1.70
II B	35	0.910	0.374	16.91	243	356	1.47
II B	40	0.967	0.441	17.14	219	403	1.83
II B	60	0.983	0.363	17.57	271	435	1.61
II B	80	0.990	0.407	17.80	243	380	1.56
III A	2.5	0.11	0.08	2.4	277	486	1.79
III A	5	0.22	0.193	4.43	227	302	1.33
III A	7.5	0.51	0.33	6.2	320	567	1.76
III A	10	0.64	0.495	7.16	259	393	1.52
III A	12.5	0.79	0.52	8.24	300	550	1.83
III A	15	0.86	0.567	8.74	303	440	1.45
III A	20	0.925	0.566	9.04	327	450	1.38
III A	25	0.945	0.651	9.41	290	441	1.52
III A	35	0.97	0.591	9.74	328	461	1.41
III A	60	0.995	0.634	2.90	314	468	1.49
III B	2.5	0.143	0.147	5.13	195	293	1.51
III B	5	0.596	0.509	6.75	234	361	1.54
III B	7.5	0.860	0.691	7.21	249	373	1.50
III B	10	0.910	0.778	7.54	230	330	1.41
III B	15	0.985	0.834	7.61	226	349	1.48
III B	20	0.99	0.820	7.64	241	350	1.45
III B	60	1.00	0.782		256	400	1.56

RUN I-A
M_0 = 1.00 g moles/liter
I_0 = 0.005 g moles/liter
Temperature = 30°C
Scavenger level = 0.0015 g moles/liter

RUN I-B
M_0 = 1.00 g moles/liter
I_0 = 0.010 g moles/liter
Temperature = 30°C
Scavenger level = 0.0015 g mole/liter

RUN II-A
M_0 = 1.0 g moles/liter
I_0 = 0.005 g moles/liter
Temperature = 40°C
Scavenger level = 0.0015 g moles/liter

RUN II-B
M_0 = 1.0 g moles/liter
I_0 = 0.10 g moles/liter
Temperature = 40°C
Scavenger level = 0.0015 g moles/liter

RUN III-A
M_0 = 1.00 g moles/liter
I_0 = 0.005 g moles/liter
Temperature = 50°C
Scavenger level = 0.0015 g moles/liter

RUN III-B
M_0 = 1.5 g moles/liter
I_0 = 0.0075 g moles/liter
Temperature = 50°C
Scavenger level = 0.0015 g moles/liter

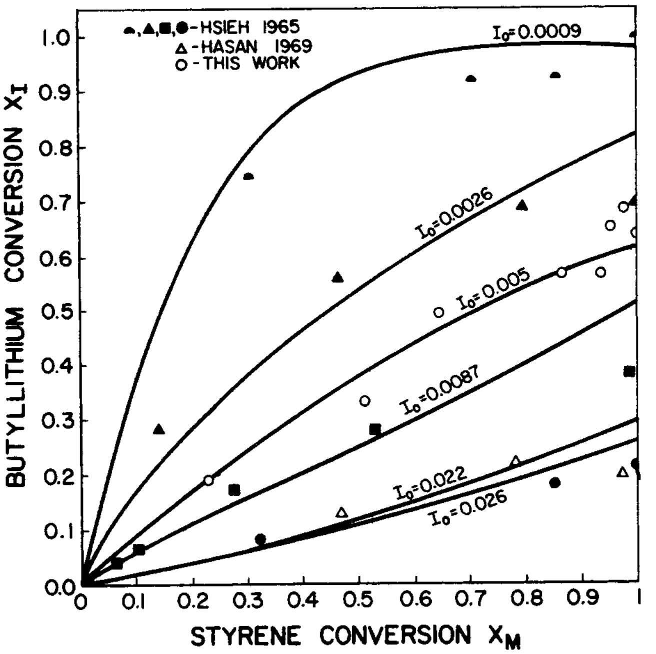

Fig. 1. Theoretical curves compared with experimental data: $[M_0]$ = 1 mole/liter; temp. = 50°C.

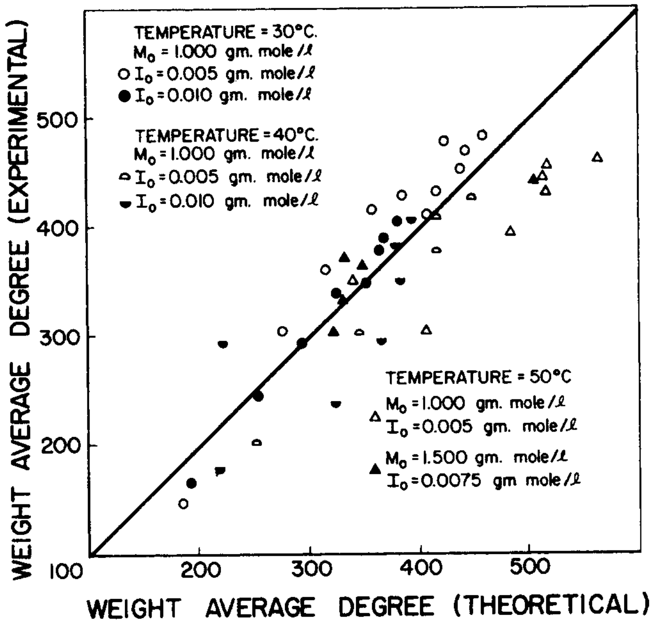

Fig. 2. Weight average degree experimental vs. weight average degree theoretical for Runs I A & B, II A & B, III A & B, 30°C, 40°C, and 50°C.

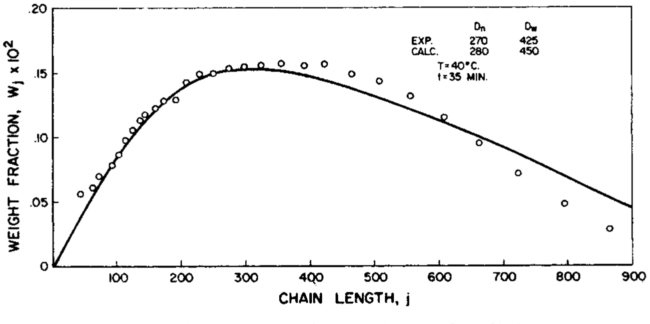

Fig. 3. Molecular weight distribution, Run II-A.

Table 2. Constants for Propagation Reaction

T°C	k' (L/m)$^{1/2}$ 1/min	k_p L/m min^{-1}	K_p
30°C	0.494 ± 5%	407	2.94×10^{-6}
40°C	1.34 ± 5%	438	18.87×10^{-6}
50°C	3.4 ± 5%	467	105.3×10^{-6}

$k' = 1.72 \cdot 10^{18} \exp(-18{,}778/RT) = k_p/\sqrt{2K_p^{-1}} = k_p\sqrt{K_p}/\sqrt{2} = A' \exp(-E'/RT)$.

$k_p = 4043 \exp(-1382/RT) = A_p \exp(-E_p/RT)$.

$K_p = 3.656 \cdot 10^{19} \exp(-34{,}790/RT) = C_T^2/A_T = \text{CONST.} \exp(-\Delta H_d/RT)$.

T°K and R = 1.9872 cal/g mole °K.

As illustrated in Figures 1, 2, and 3, good agreement was obtained between the calculated and experimental values of styrene and butyllithium conversions, molecular weights, and MWD. For those cases where the percentage deviation of calculated weight and number averages were less than 10%, the calculated MWD was a good representation of the measured MWD.

The value of k' evaluated at 30°C. is equal to the value reported by Hsieh (1965, 1966). The k' calculated at 50°C. was about 50% greater, however, as illustrated in Figure 1; the calculated conversions are in good agreement with those reported by Hsieh.

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NOTATION

A_T, C_T, P_T = concentrations of total associated, active and dead polymer
k_1, k_2, k_1', k_p, K_P = rate constants and equilibrium constants
M, I = monomer and initiator concentrations
D_n, D_w = number and weight average degree of polymerization
X_m, X_I = monomer and initiator conversions
W_j, P_j = weight fraction and concentration of polymer of j-monomer units
0 = subscript refers to initial conditions
T = temp., °K
τ = pseudo time = $\int_0^t M\,dt$ or $d\tau = M dt$

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