Application of Statistical Experimental Design in Ziegler–Natta Polymerization of Butadiene

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Synopsis

The results of butadiene polymerization initiated with $CoCl_2 \cdot 4Py/Et_2AlCl/H_2O$ are presented. The effectiveness of statistical experimental design techniques is demonstrated in identifying the individual and joint effects of polymerization variables on rate constants, molecular weights, and polydispersity. The proposed conversion model, representing polymerization with instantaneous initiation and bimolecular termination, was found to provide an adequate representation of experimental conversion data. Evidence indicates that water is not only directly involved in the initiation reaction but also plays an important role in the chain transfer reaction.

INTRODUCTION

Polymerization of butadiene initiated with $CoCl_2 \cdot 4Py/Et_2AlCl/H_2O$ has been a subject of interest in many investigations[1-5] in which the individual effects of catalyst components and temperature on the polymerization rate and molecular weight of polymer products have been fairly thoroughly studied. However, the joint effects of these reaction variables, taking account of their potential interactions, have been largely ignored. Clearly, knowledge of such joint effects is essential for a more complete characterization of any polymerization process.

The objective of this paper is to demonstrate the applicability of statistical experimental design techniques to the study of the kinetics of the above-mentioned polymerization system to determine the individual and joint effects of the reaction variables. The advantages of planning experiments with the aid of statistical design strategies have been amply demonstrated in studies of general kinetics[6] as well as other fields.[7] Nevertheless, application of these strategies in polymerization studies has not yet become common practice.

For this study polymerization was carried out in a batch reactor of 1-L capacity under a dry nitrogen atmosphere. Details of the polymerization procedure have been described by Ho.[8] Briefly, once the control of the temperature had been established, the monomer solution in toluene was added to the reactor, followed by diethylaluminum chloride (DEAC), and then the solution of cobalt catalyst. The water level in the reactor was controlled by adding water-saturated toluene. Samples were taken from the reactor at predetermined time intervals, and the monomer conversion was measured by the amount of polymer formed. The polybutadiene product was separated from the reaction mixture and its molecular weight distribution was determined using gel permeation chromatography.

EXPERIMENTAL

The operating variables selected for this study were temperature, concentration of water, and concentration of DEAC. The concentrations of cobalt and monomer were not included as variables in this study because their first-order effects on polymerization rate have been well established.

One experimental strategy, which is still commonly used to determine how different experimental conditions (operating variables) affect the rate constants and molecular weights (responses), is one-variable-at-a-time. The weakness of such a method has been well explained by Box et al.[9] This strategy provides information about the individual effects of the operating variables but not their interaction of synergistic effects. In contrast, a two-level experimental design requires fewer runs per variable studied to obtain the same information, but also reveals the joint effects of the operating variables on the responses of interest. However, since two-level designs require each operating variable to be tested at only two values, they cannot provide information about the quadratic effects of the operating variables. Some quadratic terms would be expected to be important in functional relationships between the rate constants or molecular weights and the operating variables in a system such as this one. The central composite design, originally proposed by Box and Wilson,[10] is one suitable experimental design for obtaining this more complete set of information and was selected in this work. It is an augmentation of the two-level factorial design with additional points at the central and axial positions in the operating region of interest.

A central composite design for the three operating variables in this study is shown in Figure 1 and the 15 sets of operating conditions for this design are given in Table I. The cobalt concentration and the monomer concentration were held constant at 0.11 and 1.15 mol/L, respectively, throughout this
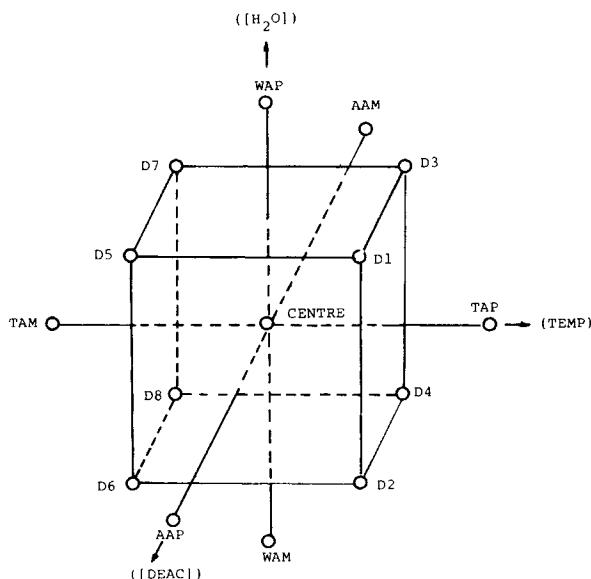

Fig. 1.   A central composite design for three variables.

TABLE I
Operating Conditions for the Central Composite Design[a]

Point	$[H_2O]$ (mmol/L)	$[Et_2AlCl]$ (mmol/L)	Temp (°C)
D1	8.95	24.28	25
D2	4.31	24.28	25
D3	8.95	14.57	25
D4	4.31	14.57	25
D5	8.95	24.28	15
D6	4.31	24.28	15
D7	8.95	14.57	15
D8	4.31	14.57	15
CENTRE	6.63	19.43	20
TAP	6.63	19.43	28.4
TAM	6.63	19.43	11.6
AAP	6.63	27.58	20
AAM	6.63	11.28	20
WAP	10.53	19.43	20
WAM	2.75	19.43	20

[a] $[Co] = 0.11$ mmol/L and $[M] = 1.15$ mol/L for all runs.

TABLE II
Percentage Conversion (%) as a Function of Time t (min)

t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
D1R1		D1R2		D2R1		D2R2		D3R1		D3R2		D4R1		D4R2	
10	12	10	13	10	11	10	3	13	8	10	8	10	23	10	27
15	16	20	22	20	19	20	18	20	9	20	8	20	38	20	44
20	20	30	29	30	26	30	25	30	12	30	15	30	50	30	55
25	21	40	36	40	33	40	30	40	12	40	16	40	55	40	64
36	30	50	43	50	40	50	37	50	15	50	17	50	66	50	71
45	34	60	48	60	45	60	41	60	17	60	20	60	71	60	75
50	38	75	56	75	52	75	46	70	18	70	22	70	77	70	80
64	45	90	62	90	54	83	49	80	19	80	23	80	78	80	81
69	47	120	81	100	56	88	52	90	20	90	24	90	82	90	84
76	50	150	85	113	58			101	21	100	27	100	82	100	87
80	51							110	22	110	26	110	84	110	89
								120	23	120	28	120	89	120	92
D5R1		D5R2		D6R1		D6R2		D7R1		D7R2		D8R1		D8R2	
10	6	10	9	10	11	10	12	10	5	10	5	10	3	10	5
21	10	20	13	20	19	13	18	20	9	20	7	20	11	20	12
30	14	30	14	31	28	17	21	30	11	30	10	30	14	30	17
40	18	40	19	39	33	20	24	40	13	40	12	40	22	40	22
50	21	50	24	50	42	24	26	60	18	50	14	50	27	50	26
60	25	60	28	61	50	29	33	70	21	70	20	60	31	55	29
70	29	70	30	65	52	36	38	91	26	80	21	71	36	60	31
80	31	80	33	70	54	44	46	100	27	90	23	75	37	65	33
91	36	90	38	73	54	48	46	110	28	100	25	79	38	71	35
100	38	100	41	79	57	54	51	120	30	110	27	83	39	75	35
110	39	110	44	83	59	58	54			120	29	88	42	80	39
120	43	120	47			61	61					92	43	85	39

TABLE II (*Continued from previous page.*)

CR1		CR2		CR3		CR4		CR5		CR6		CR7		CR8	
4	4	4	4	4	5	4	5	4	6	4	4	4	4	4	4
5	4	5	5	5	6	5	6	5	7	5	5	5	5	5	6
6	5	6	5	6	6	6	7	6	8	6	6	6	6	6	7
8	6	8	7	8	8	8	8	8	10	8	7	8	7	8	8
10	8	10	8	10	11	10	10	10	13	10	9	10	9	10	10
20	14	20	15	20	18	20	17	20	23	20	15	20	15	20	18
40	25	41	26	40	32	40	31	40	39	40	26	40	30	40	32
60	35	60	36	60	43	60	42	60	51	60	35	60	41	60	43
80	42	80	45	80	53	80	51	80	57	100	50	80	50	80	52
100	49	100	51	100	61	100	60	100	70	120	58	100	56	100	58
120	56	120	57	120	67	120	68	120	76	150	64	120	61	120	64
150	67	150	60	150	79	150	83	150	83	—	—	150	75	150	72

TAPR1		TAPR2		TAMR1		TAMR2		AAPR1		AAPR2		AAMR1	
4	7	5	9	4	3	5	4	4	4	5	5	4	3
5	9	10	16	5	4	10	8	5	5	10	3	5	3
6	10	15	23	6	4	15	11	6	6	15	10	6	4
8	12	25	34	8	5	25	17	8	7	25	24	8	5
10	14	35	43	10	5	35	23	10	9	35	32	10	7
20	24	45	50	20	9	45	29	20	15	45	39	20	13
40	40	60	58	40	17	60	36	40	26	60	48	40	23
60	51	75	64	60	23	75	42	60	36	75	55	60	31
80	60	90	69	80	29	90	47	80	43	90	59	80	37
100	68	100	76	100	35	100	50	100	51	100	62	100	42
120	74	110	77	120	40	110	52	120	56	110	65	120	47
150	82	120	86	150	47	120	55	150	64	120	71	150	43

WAPR1		WAPR2		WAMR1		WAMR2	
4	4	5	5	4	12	5	12
5	5	25	15	5	15	10	25
6	6	35	19	6	19	15	35
8	6	45	23	8	23	25	52
10	7	60	29	11	31	35	63
20	13	75	34	20	48	45	71
40	23	90	39	40	70	60	81
60	31	100	41	60	81	75	85
80	38	110	44	80	87	92	88
100	44	120	47	100	91	100	90
120	50	—	—	120	95	110	91
150	56	—	—	150	97	120	93

study. Eight replicate runs were carried out at the center point, CENTRE, and two replicate runs were performed at each of the other design points except the point AAM where only the result of one run is available. Data from replicate runs provide an estimate of experimental error variance independently of the model being fitted. Replicates at different operating conditions enable the uniformity of the error variance to be tested. The experimentally measured monomer conversion data for sampled polymerization times are given in Table II. The replicated operating conditions are denoted by R1, R2, etc. The runs were executed in random order.

CONVERSION MODEL

A polymerization reaction usually involves four fundamental steps: initiation, propagation, chain transfer, and termination (or catalyst deactivation). In formulating a conversion model the chain transfer reaction does not alter the population of active polymer molecules in the reaction mixture. In many cases, particularly in Ziegler–Natta polymerization, initiation can often be treated as an instantaneous reaction and the termination reaction may be either bimolecular or unimolecular. With these possible alternatives a variety of models can be derived based on various combinations of the polymerization steps.

However, assessment of various fitted models to preliminary experimental data in this study indicated that the only model providing an adequate representation of the conversion data was the one involving instantaneous initiation and bimolecular termination:

$$\ln([M]_i/[M]) = \left(k_p[Co^*]_i/k_{tc}[Co^*]_i\right)\ln(1 + k_{tc}[Co^*]_i t) \qquad (1)$$

where $[M]$ = monomer concentration, $[Co^*]$ = concentration of active complex, k_p, k_{tc} = rate constants for propagation and termination, respectively, t = polymerization time, and i = initial value. Subsequent analyses of the conversion model were based on eq. (1).

RESULTS AND DISCUSSION

Testing the Adequacy of the Conversion Model

Before fitting the conversion model to the experimental data, it is important to know whether the error variance is constant throughout the operating region. Bartlett's test[11] was used for that purpose.

A pooled estimate of the error variance, provided by the replicate runs at each set of operating conditions, is given by

$$S_p^2 = \left[\sum_{i=1}^{k}(m_i - 1)S_i^2\right]\bigg/\left[\sum_{i=1}^{k}(m_i - 1)\right] \qquad (2)$$

where S_i^2 = estimated error variance from the ith set of replicate runs, m_i = number of replicate runs in set i, k = number of sets of replicate runs, and S_p^2 = pooled estimate of error variance with $\sum_{i=1}^{k}(m_i - 1)$ degrees of freedom. The statistic B is then calculated as follows:

$$B = \frac{1}{C}\left\{\frac{1}{3}\left[\left(\sum_{i=1}^{k}m_i\right) - k\right]\ln S_p^2 - \sum_{i=1}^{k}(m_i - 1)\ln S_i^2\right\} \qquad (3)$$

where

$$C = 1 + \frac{\sum_{i=1}^{k}(1/m_i) - 1/\sum_{i=1}^{k}(m_i)}{3k - 3} \qquad (4)$$

The value of test statistic B is assessed using a χ^2 distribution with $k - 1$ degrees of freedom.
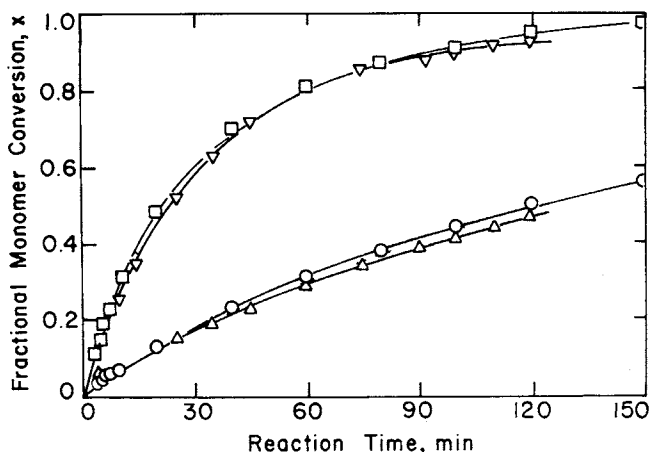
Fig. 2. Fractional monomer conversion as a function of time: (○) run WAPR1; (△) run WAPR2; (□) run WAMR1; (▽) run WAMR2.

The results of Bartlett's test for the data in Table II indicate that the replicate runs at operating conditions D4, D5, CENTRE, and TAP have different error variances than at the other operating conditions. As a consequence, weighted least squares, rather than ordinary least squares, was used to fit the conversion model (1) to the data from those runs.

Typical plots and fits of eq. (1) for monomer conversion as a function of polymerization time are shown in Figure 2.

Following fitting of eq. (1) to the data for each of the 15 operating conditions, the adequacy of each fitted model was assessed. Plots of residuals (or weighted residuals in the case of runs at D4, D5, CENTRE, and TAP) against values of $\ln([M]_i/[M])$ obtained from the fitted models were first examined. Two examples of these plots are shown in Figures 3 and 4. Figure 3
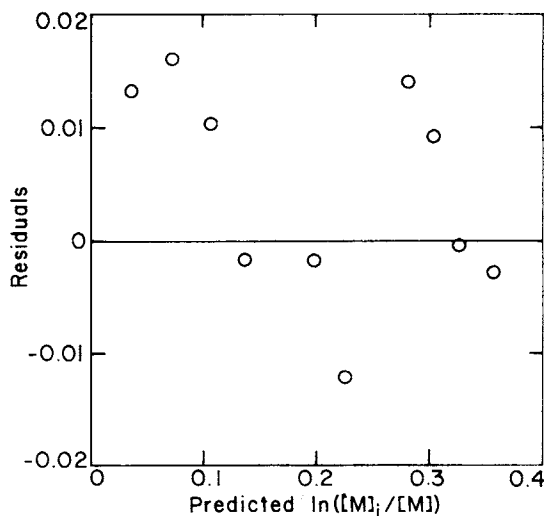

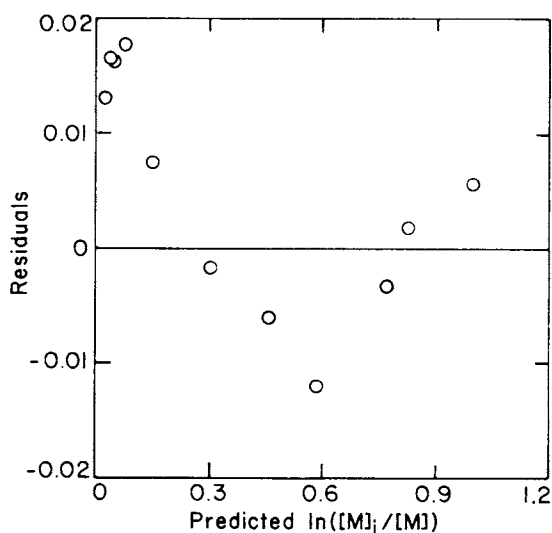Fig. 3. Residuals vs. predicted values of $\ln([M]_i/[M])$ for run D7R2.

Fig. 4. Residuals vs. predicted values of $\ln([M]_i/[M])$ for run AAPR1.

indicates no apparent systematic trend, and this was the case in most of the experimental runs. Exceptions did exist, however, such as that shown in Figure 4. For such cases a more objective statistical test of the residuals[13] was performed to determine whether or not the time sequence of residuals was random.

Defining n_1 and n_2 to be the numbers of residuals with positive and negative values, respectively, U the number of changes in sign among the residuals in the time sequence in which the data were collected, μ the mean of the discrete distribution of U, and σ^2 the variance of the discrete distribution of U, a unit normal random variable Z can be defined as

$$Z = \frac{U - \mu + 0.5}{\sigma} \qquad (5)$$

where μ and σ^2 are given by

$$\mu = \frac{2n_1 n_2}{n_1 + n_2} + 1 \qquad (6)$$

$$\sigma^2 = \frac{2n_1 n_2 (2n_1 n_2 - n_1 - n_2)}{(n_1 + n_2)^2 (n_1 + n_2 - 1)} \qquad (7)$$

Z can be evaluated for the set of residuals from each experimental run. The probability of a particular value of Z can then be obtained from a normal distribution table, and the value of that probability can indicate whether or not the residuals for that particular run behave randomly. A probability level of 0.05 was chosen in this study as a level of significance for this test. In other words, any set of residuals that produced a calculated probability greater than 0.05 would be considered to have a random arrangement.

TABLE III
Estimates of Rate Parameters and Associated Standard Deviations

| Expt. no. | $k_p[Co^*]_i$ (s^{-1}) | | | $k_{tc}[Co^*]_i$ (s^{-1}) | | |
	Estimated parameter $\times 10^4$	Estimated standard deviation $\times 10^5$	df	Estimated parameter $\times 10^4$	Estimated standard deviation $\times 10^5$	df
D1(R1, R2)	1.81	1.62	8	0.40	4.89	8
D2(R1, R2)	1.87	1.28	8	1.52	4.44	9
D3(R1, R2)	1.19	2.29	11	9.23	32.52	11
D4(R1, R2)	5.73	3.19	9	3.18	5.52	9
D5(R1, R2)	0.87	0.40	11	0.32	1.84	11
D6(R1, R2)	2.57	2.82	11	1.85	9.34	11
D7(R1, R2)	0.61	0.37	11	0.93	2.51	11
D8(R1, R2)	1.02	0.42	10	0.04	1.98	10
CENTRE(R1, R2, R3, R4, R5, R6 R7, R8)	1.74	0.94	43	1.01	2.80	43
TAP(R1, R2)	3.13	1.37	8	1.89	3.48	9
TAM(R1, R2)	1.35	2.89	11	1.55	11.42	11
AAP(R1, R2)	2.07	3.56	9	1.87	10.98	10
AAM(R1)	1.17	0.20	5	0.98	0.77	5
WAP(R1, R2)	1.07	0.49	10	0.78	2.34	10
WAM(R1, R2)	5.19	2.49	11	1.60	2.75	11

Using this test, the residuals in runs TAPR1, TAMR1, AAPR1, and WAPR1 were found to have systematic time trends. Residual sequences in all other runs were found to be random. There was no apparent cause for the residuals in those four runs to display systematic behavior, particularly since the residuals from each associated replicate run indicated no such time dependence. One possible cause might be that 30–45 s are required to withdraw a sample solution from the reactor and quench the reaction. For those four runs having nonrandom residuals, nearly half of the data points were taken during the very early stage of polymerization in order to obtain more information about the initiation step. Each recorded sampling time might have lagged the actual polymerization time by as much as 40 s. This problem would be particularly serious at the early stage of the reaction where the polymerization rate is high and the monomer conversion is low, and could therefore affect the conversion results. This might also explain why large positive residuals were frequently observed in a number of preliminary samples where time dependence was found.

Statistical evaluation of the adequacy of the fitted conversion model was also carried out using a lack of fit test.[12] In this test, the ratio of the variance due to lack of fit to the variance due to pure error calculated from replicates is compared with the appropriate F-distribution. For all runs the calculated ratios were found to be nonsignificant, indicating that there was no evidence to suggest any inadequacy in the proposed conversion model under the experimental conditions studied.

The conversion model (1) was fitted to the combined data from the two replicate runs at each set of operating conditions. Table III presents the estimates of the parameters and their standard deviations for all experimental conditions.

Relating the Rate Constants to the Operating Conditions

The dependence of each of the estimated rate parameters, $k_p[\text{Co}^*]_i$ and $k_{tc}[\text{Co}^*]_i$, as a function of the three operating variable, was developed empirically using a full second-degree polynomial. In developing these equations a larger body of experimental data was used, including preliminary experimental runs as well as the replicated runs of the central composite design.

Before fitting empirical models to the estimated rate constants, the consistency of the variances of individual rate constants was checked using Bartlett's test over all of the experimental runs. The results of this exercise indicated that these variances changed with operating conditions and so weighted least squares was employed.

A full second degree polynomial model was fitted first for each of the rate constants:

$$\hat{k} = B_0 + B_1 T + B_2[\text{H}_2\text{O}] + B_3[\text{DEAC}] + B_4 T^2 + B_5[\text{H}_2\text{O}]^2$$

$$+ B_6[\text{DEAC}]^2 + B_7 T[\text{H}_2\text{O}] + B_8 T[\text{DEAC}] + B_9[\text{H}_2\text{O}][\text{DEAC}] \quad (8)$$

where $\hat{k}$ is the estimated rate constant (k_p or k_{tc}) from the conversion model

Estimates of Parameters and Associated Standard Deviations for the
Empirical Models for the Rate Constants

Rate constant		Parameter estimate	Estimated standard deviation	t Ratio (parameter estimate/ standard deviation)
$\hat{k}_p[\text{Co}^*]_i$	B_1	4.50×10^{-5}	1.64×10^{-5}	2.75
	B_2	-2.42×10^{-4}	8.23×10^{-5}	-2.94
	B_5	7.71×10^{-6}	5.07×10^{-6}	1.52
	B_7	-1.67×10^{-6}	7.99×10^{-7}	-2.09
	B_9	4.97×10^{-6}	2.38×10^{-6}	2.09
$\hat{k}_{tc}[\text{Co}^*]_i$	B_3	1.55×10^{-4}	4.83×10^{-5}	3.21
	B_4	1.62×10^{-6}	1.03×10^{-6}	1.58
	B_7	-8.78×10^{-6}	3.23×10^{-6}	-2.72
	B_8	-5.46×10^{-6}	1.94×10^{-6}	-2.81
	B_9	-8.64×10^{-6}	3.34×10^{-6}	-2.59

(1), B_i, $i = 1, \ldots, 9$, are regression coefficients, and T is the temperature ($°C$). After dropping the insignificant terms from the fitted equation (8), reduced models were fitted to the data. The final fitted empirical models were as follows:

$$\hat{k}_p[\text{Co}^*]_i = 5.46 \times 10^{-4} + B_1 T + B_2[\text{H}_2\text{O}] + B_5[\text{H}_2\text{O}]^2$$

$$+ B_7 T[\text{H}_2\text{O}] + B_9[\text{H}_2\text{O}][\text{DEAC}] \tag{9}$$

$$\hat{k}_{tc}[\text{Co}^*]_i = -1.44 \times 10^{-3} + B_3[\text{DEAC}] + B_4 T^2 + B_7 T[\text{H}_2\text{O}]$$

$$+ B_8 T[\text{DEAC}] + B_9[\text{H}_2\text{O}][\text{DEAC}] \tag{10}$$

Parameter estimates for eqs. (9) and (10) along with their estimated standard deviations and t ratios are given in Table IV. For the propagation rate constant k_p the individual effects of two of the operating variables, temperature and water content, can be seen to be slightly more important than those due to the interaction terms. It has been commonly observed by previous workers[13,14] that there exists a maximum in the plot of polymerization rate vs. [H_2O]. Since the water concentrations studied in this work are higher than those reported in the above references, the decrease in $k_p[\text{Co}^*]_i$ with an increase in [H_2O] is reasonable.

Previous work has also shown that the [H_2O]/[DEAC] ratio has a strong influence on the polymerization rate. The results of this study support that finding since the pattern of the change in k_p with [H_2O]/[DEAC] are consistent with these previously reported.

Correlation of M_n, M_w, and PD

Number and weight averages of molecular weights (M_n and M_w) and polydispersity (PD = M_w/M_n) were determined at a number of conversions for the polymer products from the eight operating conditions at the "corner
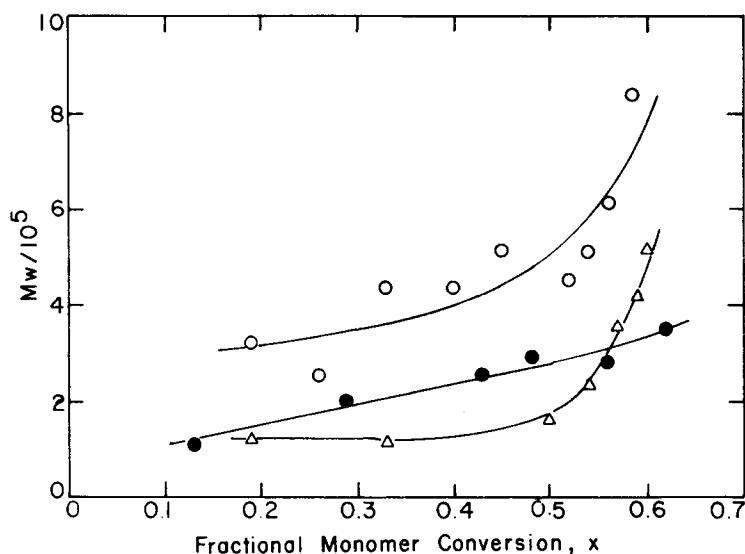
Fig. 5. Weight average molecular weight M_w as a function of fractional monomer conversion x: (○) run D2R1; (●) run D1R4; (△) run D6R1.

positions" of the central composite experimental design (conditions D1–D8). At each of the axial positions of the design only one sample, at about 27% conversion, was taken.

Figure 5 shows the general behavior of M_w as a function of monomer conversion. M_w increases slowly initially with fractional monomer conversion, and then increases more rapidly near the end of the polymerization reaction (approximately 2 h). The polydispersity increases with monomer conversion to a maximum, and then, when M_w begins to increase sharply, PD begins to decrease. Similar results have been obtained by Yang and Hsu[15] for the catalyst system $Co(acac)_3/Al(i\text{-}Bu)_3/H_2O$ and by Hsu and Ng[4] for the same catalyst used in this work but at lower water and DEAC concentrations. The molecular weight distributions of many polybutadiene samples in the current study were found to possess a shoulder peak in the high molecular weight region. For those samples which did not have a shoulder peak, the distribution curves declined linearly at high molecular weights. These observations support the bimolecular termination reaction inferred from fitting the conversion model. At the initial stage of polymerization, termination by combination is relatively less important than propagation; but the significance of the termination reaction increases with conversion and becomes even more important relative to propagation towards the end of polymerization. Indeed, in this study shoulder peaks were found to be more prevalent for those samples taken at high monomer conversions.

The influence of temperature and compositions of catalysts have been studied previously under controlled conditions by other researchers.[1-5, 14,15] But those reports considered the individual rather than the joint effects of those factors. In this study it has been demonstrated that, with the help of an appropriate statistical experimental design, the individual and joint effects of these variables can be studied effectively with minimum effort.

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TABLE V
M_w, M_n, and PD Measured at About 27% Monomer Conversion

Expt. no.	Fractional monomer conversion	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	PD
D1R1	0.25	1.95	3.44	5.66
D1R2	0.30	1.48	3.34	4.43
D2R1	0.26	2.07	4.32	4.80
D2R2	0.25	2.56	7.41	3.46
D3R2	0.25	2.19	3.91	5.58
D4R2	0.26	0.90	2.28	3.96
D5R1	0.25	1.40	2.88	4.85
D6R2	0.27	1.92	5.68	3.37
D7R2	0.25	1.48	3.65	4.05
D8R2	0.27	1.82	5.27	3.45
CENTRE R3	0.27	2.98	5.92	5.04
CENTRE R6	0.24	2.04	2.68	7.59
CENTRE R8	0.30	3.31	7.13	4.65
TAPR2	0.24	1.30	1.75	7.43
TAMR2	0.24	0.78	2.47	3.18
AAPR2	0.25	1.53	3.84	3.98
AAMR1	0.24	0.41	1.69	2.45
WAPR1	0.24	0.18	0.76	2.36
WAMR1	0.24	0.95	2.08	4.57

As an illustration consider the molecular weight and PD data at approximately 27% monomer conversion as given in Table V. These data were chosen from experiments at each of the 15 operating conditions in the central composite design. As in the empirical modeling of the rate constants, full second-degree polynomial models of the form of eq. (8) were fitted to M_w, M_n, and PD as functions of T, [H_2O], and [DEAC]. Nonsignificant terms in the fitted models were then deleted, and the reduced model forms were refitted to the data. The final models are given by eqs. (11)–(13), and the estimated parameter values with corresponding standard deviations and t ratios are given in Table VI.

$$M_w = -1.39 \times 10^6 + B_1 T + B_2 [H_2O] + B_3 [DEAC]$$

$$+ B_4 T^2 + B_5 [H_2O]^2 + B_6 [DEAC]^2 \tag{11}$$

$$M_n = -1.11 \times 10^6 + B_1 T + B_2 [H_2O] + B_3 [DEAC] + B_4 T^2$$

$$+ B_5 [H_2O]^2 + B_6 [DEAC]^2 \tag{12}$$

$$PD = -13.99 + B_2 [H_2O] + B_3 [DEAC] + B_5 [H_2O]^2$$

$$+ B_6 [DEAC]^2 \tag{13}$$

These equations indicate that the behavior of the molecular weights and polydispersity can be described by the individual effects of the operating variables alone since none of the interactions between variables were found to be significant.

TABLE VI
Estimates of Parameters and Associated Standard Deviations for
the Empirical Models for M_w, M_n, and PD

Model		Parameter estimate	Estimated standard deviation	t Ratio
M_w	B_1	6.18×10^4	3.68×10^4	1.68
	B_2	1.16×10^5	5.69×10^4	2.04
	B_3	6.30×10^4	3.80×10^4	1.66
	B_4	-1.39×10^3	9.15×10^2	-1.52
	B_5	-9.58×10^3	4.20×10^3	-2.28
	B_6	-1.58×10^3	9.63×10^2	-1.64
M_n	B_1	8.09×10^3	9.99×10^3	0.81
	B_2	1.34×10^4	1.54×10^4	0.87
	B_3	4.22×10^3	1.03×10^4	0.41
	B_4	-1.89×10^2	2.49×10^2	-0.76
	B_5	-1.33×10^3	1.15×10^3	-1.16
	B_6	-1.01×10^2	2.62×10^2	-0.38
PD	B_2	1.76	9.89×10^{-1}	1.78
	B_3	1.34	6.63×10^{-1}	2.02
	B_5	-1.28×10^{-1}	7.40×10^{-2}	-1.73
	B_6	-3.30×10^{-2}	1.68×10^{-2}	-1.96

As can be seen from Table VI, among the three variables tested the concentration of water is the most prominent controlling factor for M_w. The combined effects of the first and second order terms in water concentration indicate that M_w passes through a maximum value within the range studied. Molecular weights of samples taken at approximately the same conversion in several similar systems[3,14] were reported to increase with water content. It should be noted, however, that the present data were obtained at higher water concentrations, up to 11 mmol/L, than those in the previous studies which were well below 6 mmol/L. The results obtained in the present study agree with those reported by Zgonnik.[5]

It is believed that water not only participates in the initiation reaction but also plays an important role in the chain transfer reaction upon which PD depends. The significant effects of the concentrations of water and DEAC in the fitted model (13) for PD support this conjecture. According to this empirical model, PD passes through a maximum as the concentration of either water or DEAC increases over the operating ranges studied.

Increases in the polymerization temperature and the concentration of DEAC over the ranges studied were both found to cause M_w to pass through a maximum. The net effects are small, however, and agree with the results obtained by Bawn[1] for a $Co(acac)_3/Et_2AlCl/H_2O$ catalyst over a range of DEAC concentrations from 2.5 to 10.0 mmol/L.

The nonsignificant values of all of the parameter estimates in the fitted empirical model (12) for M_n can be attributed to the large scatter in the molecular weight data.

CONCLUSION

In this study of the polymerization of butadiene initiated with $CoCl_2$ $4Py/Et_2AlCl/H_2O$ catalyst, the effectiveness of statistical experimental de-

sign techniques has been demonstrated in identifying the individual and joint effects of polymerization variables on rate constants, molecular weights, and polydispersity. Clearly this approach can also be applied to other polymerization systems or more generally to other processes.

Monomer conversion data as a function of polymerization time have also been presented. The proposed conversion model, representing polymerization with instantaneous initiation and bimolecular termination or catalyst deactivation, was found to provide an adequate representation of these data.

References

1. C. H. E. Bawn, *Rubber Plast. Age*, **46**, 510 (1965).

2. V. S. Byrikhin, V. A. Tverskoi, S. S. Potapov, N. N. Luzina, and N. P. Fedorov, *Polym. Sci. U.S.S.R.*, **58**, 1222 (1974).

3. M. Gippin, *Ind. Eng. Chem., Prod. Res. Dev.*, **1**(1), 3 (1962).

4. C. C. Hsu and L. Ng, *AIChE J.*, **22**, 66 (1976).

5. V. N. Zgonnik, B. A. Dolgoplosk, N. I. Nikolayev, and V. A. Kropachev, *Polym. Sci. U.S.S.R.*, **7**(2), 338 (1965).

6. G. E. P. Box and P. V. Youle, *Biometrices*, **11**, 289 (1955).

7. W. J. Hill and W. G. Hunter, *Technometrics*, **8**, 289 (1966).

8. F. K. W. Ho, M.Sc. thesis, Queen's University, Kingston, Ontario, Canada, 1982.

9. G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, Wiley, New York, 1978, Chap. 15.

10. G. E. P. Box and K. B. Wilson, *J. Roy. Stat. Soc.*, **B13**, 1 (1951).

11. M. S. Bartlett, *Proc. Roy. Soc. A*, **160**, 268 (1937).

12. N. Draper and H. Smith, *Applied Regression Analysis*, 2nd ed., Wiley, New York, 1981.

13. L. V. Gavrilova, J. A. Gechanoskii, Ye. N. Kropacheva, and B. A. Dolgoplosk, *Polym. Sci. U.S.S.R.*, **10**(9), 2324 (1968).

14. I. Velea, V. Dimonie, E. Melege, P. Blenka, and V. Provinceanu, *Rev. Roumaine Chim.*, **14**, 473 (1969).

15. W. L. Yang and C. C. Hsu, *J. Appl. Polym. Sci.*, **28**, 145 (1983).