Fundamental Modeling in Anionic Polymerization Processes

C. C. CHANG, J. W. MILLER, JR., and G. R. SCHORR,

The Goodyear Tire & Rubber Company, Akron, Ohio 44305

Synopsis

The anionic solution polymerization of butadiene was studied employing both batch and continuous reactor operations with n-butyllithium (n-BuLi) initiator, tetramethylethylenediamine (TMEDA) modifier, and hexane solvent. A model was proposed that described the kinetics as a function of both the fully modified and unmodified regressed rate data. Using the proposed kinetic model, the conversion, vinyl structure, and heterogeneity index of polymers produced for a series of continuous runs were successfully predicted. The model was used to simulate several process configurations.

INTRODUCTION

Ziegler-Natta catalysts are used widely to produce elastomers of given stereo-specific microstructure under conditions of relative insensitivity to process variations and environmental impurities. However, polymer architecture is difficult to customize for new or unique applications. Research into living anionic polymerization systems, notably lithium, has recently undergone a renaissance as polymer chemists have identified applications for highly customized polymer architectures. Specifically, the tire and rubber industry has tailormade elastomers of controlled molecular weight (MW), molecular weight distribution (MWD), microstructure, sequence distribution, and branching, in order to meet today's tire requirements for traction, treadwear, and rolling resistance.

The need to control so many process variables presents problems of reproducibility and scale-up to the research chemist and process engineer alike. Lithium systems are sensitive to polar impurities, the microstructure varies with temperature, and both microstructure and sequence distribution can vary with small changes in catalyst modifier. Ranges of sequence length and molecular weight distributions, as well as production capacity and cost, are defined to a large extent by the type and configuration of the reactor system selected.

This challenge has been met by incorporating fundamental process analysis at an early stage in new elastomer development. Small-scale reactor systems with state-of-the-art computer process controls enable precise control and data acquisition. These data are used to analyze process sensitivity and to develop kinetic models and continuous reactor models that accurately predict conversion, microstructure, and molecular weights and distributions as a function of process and chemistry variables. These models have become an important and necessary part of the scale-up procedure.

CHANG, MILLER, AND SCHORR

This work details the development and application of polymerization process models for a basic and nonproprietary system, and demonstrates the benefits derived from this engineering approach. The polymerization system chosen for this work is of broad interest as it utilizes some of the most common commercial materials; butadiene (Bd) monomer, n-BuLi initiator, TMEDA modifier, and hexane solvent. The solvent for this system was chosen additionally because of its minimal effect on the catalyst.

BACKGROUND

The mechanism of polymerization of conjugated dienes with alkyllithium initiators including n-BuLi has been extensively studied. Recent reviews on this subject are presented by Young et al.[1] and Van Beylen et al.[2] The exact mechanism of the butadiene propagation remains a topic of debate, with kinetic orders of the 1/6, 1/4, 1/3, and 1/2 power of butadienyllithium concentration reported in the literature. The differences in kinetic order may be explained, in part, by the specific combinations of initiator and solvents (affecting the degree of association), and by differences in initiator concentration and reaction temperature (affecting the association equilibrium and thus the kinetics).
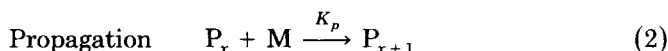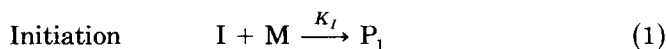
A summary of pertinent published kinetic work is shown in Table I, where it can be seen that most of the studies looked at the kinetic order or the degree of association but did not report complete kinetic data such as activation energy and frequency factor. Nor is sufficient raw data reported from which these parameters may be calculated.

As can be seen in Table I, there are two reaction systems similar to the model system chosen; one with and one without TMEDA. Pioneer work on unmodified PBD polymerization was carried out by Morton et al.[3-6]; a kinetic order of 1/4 was reported. For highly modified PBD polymerization, Hay and co-workers[7] reported a kinetic order of 1.0 and activation energy of 3500 cal/mol with the TMEDA to n-BuLi ratio fixed at 2.2. However, the initiator concentration ranged from 27 to 69 mmol/L; much higher than the 0.5 to 0.8 mmol/L investigated by the authors. Similarly, the reaction temperature range was limited at $-40°C$ to $-22°C$; much below the area of commercial interest.

Information on partially modified systems (below 1:1 mole ratio modifier:lithium) is of major interest because of the tremendous variability in microstructure possible. Published information in these critical areas is absent due to the precision required in collecting data and the effort required to explain and model the incremental changes in kinetic rate and polymer microstructure.

DEVELOPMENT OF THE KINETIC MODEL

Generally, the mechanism of an anionic living polymerization without termination and chain transfer reactions is expressed as:

$$\text{Initiation} \qquad \text{I} + \text{M} \xrightarrow{K_I} \text{P}_1 \qquad (1)$$

$$\text{Propagation} \qquad \text{P}_x + \text{M} \xrightarrow{K_p} \text{P}_{x+1} \qquad (2)$$

where $x = 2, 3, \ldots$.

TABLE I
Published Kinetic Data of PBD Polymerization

$$-d[M]/dt = K[I]_0^n[M]$$
$$= K_0 \text{EXP}(-E/RT)[I]_0^n[M]$$

I	[I] (mmol/L)	n	E (cal/mol)	K_0	Reference
n-Hexane solvent					
n-BuLi	0.9–12	0.5	21500	?	3, 4, 5
n-BuLi	0.2–17	0.25	?	?	6
n-Hexane solvent with TMEDA modifier					
n-BuLi	27–68	1.0	3500	$6.3 \times 10E4$	7
Cyclohexane solvent					
n-BuLi	0.4–10	0.167	?	?	8
s-BuLi	> 10	0.5	?	?	9, 10, 11, 12
s-BuLi	0.1–10	0.333	?	?	9, 10, 11, 12
s-BuLi	0.021–0.89	0.3–0.4	15600–19800	?	13
n-Heptane solvent					
s-BuLi	0.039–0.96	0.2–0.4	17800–21400	?	13
Benzene solvent					
n-BuLi	1.0–10	0.167	?	?	6
Toluene solvent					
s-BuLi	0.030–0.90	0.2–0.3	14300–19700	?	13
THF solvent					
n-BuLi	0.6–2.2	1.0	6100	$4.3 \times 10E4$	3, 4, 5
Results of this work					
Mixed hexane solvent					
n-BuLi	0.16–0.92	0.334	19306	$1.994 \times 10E12$	
Mixed hexane solvent with TMEDA modifier					
n-BuLi	0.33–1.03	1.0	10332	$7.024 \times 10E8$	

Results of viscosity measurements[5] indicated that living polybutadiene polymers may form aggregates in the solution especially in the absence of modifier. This will greatly affect the kinetics of the polymerization, thus, the following reaction needs to be included:

$$\text{Association} \qquad a\text{P}_d \xleftrightarrow{K_a} \text{P}_a \qquad (3)$$
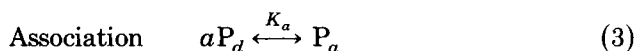
In the above equations, M is the monomer (butadiene), I is the initiator (n-BuLi), P(x) is the polymer having chain length x, P_d and P_a are the dissociated and associated polymer, and a is the degree of association. K_I and K_P are the rate constants of the initiation and propagation reactions, respectively; while K_a is the equilibrium constant of the association reaction.

Morton[6] argues that the kinetic order may not necessarily reflect the state of association of the active polymer chains; he determined a kinetic order of 1/4 with respect to initiator, but claims a dimeric structure based upon viscosity measurements of the living polymer. Worsfold and Bywater[14] reported that the association number is 4 based on a light scattering method, and Glaze and co-workers[15] reported that the association number is 2 to 4 (concentration dependent) based on a cryoscopy method. In this work, the authors will test a model assuming that there is only one associated state and

that it can be related to the kinetic order. If, indeed, the living polymer can exist in multiple associated states, the regressed kinetic order would represent the "effective" or "average" association number.

From eq. (3), the concentration of dissociated polymer can be related to concentration of total polymer by

$$[P] = [P_d] + a[P_a] = [P_d] + aK_a[P_d]^a \qquad (4)$$

For a highly associated polymer, we have

$$[P_d] = (aK_a)^{-1/a}[P]^{1/a} \qquad (5)$$

In the above equations, $[P_d]$, $[P_a]$, and $[P]$ are the concentration of dissociated polymer, concentration of associated polymer, and concentration of total polymer, respectively; i.e.,

$$[P_d] = \sum_{x=1}^{\infty} [P_{xd}] \qquad (6)$$

$$[P_a] = \sum_{x=1}^{\infty} [P_{xa}] \qquad (7)$$

$$[P] = \sum_{x=1}^{\infty} [P_x] \qquad (8)$$

It is assumed that the associated polymer is dormant for propagation and is in equilibrium with the active dissociated polymer. It is also assumed that the ratio of dissociated polymer to total polymer, h, is constant at each chain length, i.e.,

$$h = \frac{[P_{1d}]}{[P_1]} = \frac{[P_{2d}]}{[P_2]} = \cdots = \frac{[P_{xd}]}{[P_x]} \qquad (9)$$

Summing this relationship and combining with eq. (5) gives the following expression:

$$h = \frac{(aK_a)^{-1/a}[P]^{1/a}}{[P]} \qquad (10)$$

In order to derive equations which can be used for both an unmodified system and a fully modified system, K_p is defined as:

$$K_p = K_{pu}h \qquad \text{Unmodified system} \qquad (11)$$

$$= K_{pm}1 = K_{pm} \qquad \text{Fully modified} \qquad (12)$$

$$= fK_{pm} + (1 - f)K_{pu}h \qquad \text{Partially modified} \qquad (13)$$

The unmodified system has the term h to convert total polymer concentration to dissociated polymer concentration in the propagation kinetic expression. A fully modified system is defined as one in which all living polymers are complexed with the modifier and exist in dissociated form ($h = 1$). A partially modified system is assumed to contain a mixture of modified and unmodified living polymers. The rate of polymerization and microstructure of polymer produced can be determined by the contributions of the two parallel and competing polymerizations. The fraction of polymer which forms a complex with TMEDA is defined as f and eq. (13) describes the overall propagation constant.

The rate of initiation, propagation reactions, and the rate of monomer consumption (or rate of polymerization) based on the proposed mechanism are

$$-\frac{d[\mathrm{I}]}{dt} = K_I[\mathrm{I}][\mathrm{M}] \tag{14}$$

$$\frac{d[\mathrm{P}_1]}{dt} = K_I[\mathrm{I}][\mathrm{M}] - K_p[\mathrm{P}_1][\mathrm{M}] \tag{15}$$

$$\frac{d[\mathrm{P}_x]}{dt} = K_p[\mathrm{P}_{x-1}][\mathrm{M}] - K_p[\mathrm{P}_x][\mathrm{M}] \tag{16}$$

$$-\frac{d[\mathrm{M}]}{dt} = K_I[\mathrm{I}][\mathrm{M}] + K_p[\mathrm{P}][\mathrm{M}] \tag{17}$$

For the polymerization of butadiene, the initiation is very fast in hexane even in the absence of modifier. This is also supported by our experimental conversion data. Therefore, the initiation reaction can be assumed to be instantaneous and the equations for molecular weight distribution can be simplified to

$$\frac{d[\mathrm{P}_1]}{dt} = -K_p[\mathrm{P}_1][\mathrm{M}] \tag{18}$$

$$\frac{d[\mathrm{P}_x]}{dt} = K_p[\mathrm{P}_{x-1}][\mathrm{M}] - K_p[\mathrm{P}_x][\mathrm{M}] \tag{19}$$

It can generally be assumed that the amount of monomer consumed in the initiation reaction is negligible (long-chain approximation). Thus, the equation for rate of polymerization is reduced to

$$-\frac{d[\mathrm{M}]}{dt} = K_p[\mathrm{P}][\mathrm{M}] \tag{20}$$

where $[\mathrm{P}] = [\mathrm{I}]_0$ the initial concentration of n-BuLi.

DEVELOPMENT OF REACTOR MODELS

Batch or Plug Flow Reactor

The governing equations of a batch or plug flow reactor are the same as those described in the kinetic model [eqs. (18)–(20)] with initial conditions:

$$[P_1] = [I]_0$$

$$[P_x] = 0$$

$$[M] = [M]_0$$

If the parameters are known, the above equations can be solved to give the concentration of monomer, [M], and concentration of polymer having chain length x, $[P_x]$, at any time after initiation. These can then be converted to conversion and molecular weight distribution.

Solving for monomer concentration [eq. (20)] gives

$$[M] = [M]_0 e^{-K_p[I]_0 t} \tag{21}$$

or in terms of monomer conversion, X, as:

$$X = 1 - e^{-K_p[I]_0 t} \tag{22}$$

To obtain the molecular weight distribution, equations for polymer chains, $[P_x]$, need to be solved. A commonly used approach is to linearize the infinite set of differential equations by employing the "eigenzeit" transformation[16, 17] as shown below:

$$dz = K_p[M]\, dt \tag{23}$$

The solution for z is

$$z = \frac{[M]_0 - [M]}{[I]_0} \tag{24}$$

which is the average number of monomer units added per initiating molecule, or more commonly, the average degree of polymerization. The linearized equations of the polymer chain are

$$-\frac{d[P_1]}{dz} = [P_1] \tag{25}$$

$$\frac{d[P_x]}{dz} = [P_x] - [P_{x-1}] \tag{26}$$

The polymer chains are functions of z only and can be solved analytically by

induction. The solution takes the form of a Poisson distribution as follows:

$$Y_x = \frac{[P_x]}{[I]_0} = \frac{e^{-z}z^{x-1}}{(x-1)!} \tag{27}$$

where Y_x is the mole fraction distribution of the polymer. The number-average and weight-average chain lengths (X_n/X_w) or number-average and weight-average molecular weights (M_n/M_w) can be calculated from this distribution as:

$$X_n = \frac{M_n}{F_w} = \frac{\sum\limits_{x=1}^{\infty} xY_x}{\sum\limits_{x=1}^{\infty} Y_x} = 1 + z \tag{28}$$

$$X_w = \frac{M_w}{F_w} = \frac{\sum\limits_{x=1}^{\infty} x^2Y^x}{\sum\limits_{x=1}^{\infty} xY_x} = \frac{1 + 3z + z^2}{(1 + z)} \tag{29}$$

where F_w is the molecular weight of the monomer.
The heterogeneity index, HI, is

$$HI = \frac{M_w}{M_n} = \frac{1 + 3z + z^2}{(1 + z)^2} \tag{30}$$

It can be shown from the above equation that HI decreases rapidly toward 1 at high molecular weight (e.g., 1.083 for $X_n = 10$ and 1.010 for $X_n = 100$) in the absence of initiation and termination effects.

Continuous Stirred Tank Reactors (CSTR) in Series

The governing equations of a series of continuous stirred tank reactors were derived with the following assumptions: (a) all reactors are completely mixed, (b) each reactor is under isothermal condition, and, as a first approximation, (c) density changes can be neglected.
The mass balances for species A are of the form (e.g., Bird et al.[18]):

(rate of accumulation of A) = (rate of mass of A in) − (rate of mass of A out) − (rate of disappearance of A by reaction)

For the j-th reactor, the mass balances for monomer and polymers are

$$V_j \frac{d[\mathrm{M}]_j}{dt} = F[\mathrm{M}]_{j-1} - F[\mathrm{M}]_j - V_j R_{\mathrm{M},j} \tag{31}$$

$$V_j \frac{d[\mathrm{P}_1]_j}{dt} = F[\mathrm{P}_1]_{j-1} - F[\mathrm{P}_1]_j - V_j R_{\mathrm{P1},j} \tag{32}$$

$$V_j \frac{d[\mathrm{P}_x]_j}{dt} = F[\mathrm{P}_x]_{j-1} - F[\mathrm{P}_x]_j - V_j R_{\mathrm{P}x,j} \tag{33}$$

respectively. In the above equations, F is the volumetric flow rate, V_j is the volume of j-th reactor, and the j appearing in the concentration and rate expressions refers to the value of that variable at the j-th reactor. The rate expressions are the same as those described in the polymerization kinetics, eqs. (10)–(20). Substituting those expressions in the above equations and introducing the reactor mean residence time, $\tau_j = V_j/F$, we have

$$\frac{d[\mathrm{M}]_j}{dt} = \frac{[\mathrm{M}]_{j-1} - [\mathrm{M}]_j}{\tau_j} - K_{P,j}[\mathrm{I}]_0[\mathrm{M}]_j \tag{34}$$

$$\frac{d[\mathrm{P}_1]_j}{dt} = \frac{[\mathrm{P}_1]_{j-1} - [\mathrm{P}_1]_j}{\tau_j} - K_{P,j}[\mathrm{P}_1]_j[\mathrm{M}]_j \tag{35}$$

$$\frac{d[\mathrm{P}_x]_j}{dt} = \frac{[\mathrm{P}_x]_{j-1} - [\mathrm{P}_x]_j}{\tau_j} + K_{P,j}[\mathrm{P}_{x-1}]_j[\mathrm{M}]_j$$

$$- K_{P,j}[\mathrm{P}_x]_j[\mathrm{M}]_j \tag{36}$$

This set of dynamic ordinary differential equations can be solved to yield the conversion and polymer molecular weight distribution at the outlet of any reactor if the parameters and operating conditions are known.

At steady state, the above equations [eqs. (34)–(36)] reduce to a set of algebraic equations, which can be easily solved, as shown below:

$$[\mathrm{M}]_{j-1} - [\mathrm{M}]_j - \tau_j K_{P,j}[\mathrm{I}]_0[\mathrm{M}]_j = 0 \tag{37}$$

$$[\mathrm{P}_1]_{j-1} - [\mathrm{P}_1]_j - \tau_j K_{P,j}[\mathrm{P}_1]_j[\mathrm{M}]_j = 0 \tag{38}$$

$$[\mathrm{P}_x]_{j-1} - [\mathrm{P}_x]_j + \tau_j K_{P,j}[\mathrm{P}_{x-1}]_j[\mathrm{M}]_j - \tau_j K_{P,j}[\mathrm{P}_x]_j[\mathrm{M}]_j = 0 \tag{39}$$

For concentration of monomer, the solution is

$$\frac{[\mathrm{M}]_j}{[\mathrm{M}]_{j-1}} = \frac{1}{1 + K_{P,j}[\mathrm{I}]_0 \tau_j} \tag{40}$$

or in terms of conversion of initial monomer concentration:

$$1 - X_j = \frac{[M]_j}{[M]_0} = \frac{[M]_1[M]_2 \cdots [M]_j}{[M]_0[M]_1 \cdots [M]_{j-1}}$$

$$= \frac{1}{(1 + K_1\tau_1)(1 + K_2\tau_2) \cdots (1 + K_j\tau_j)} \tag{41}$$

where X_j is the conversion of monomer from the j-th reactor, and $K = K_P[I]_0$.

For the molecular weight distribution, eqs. (38) and (39) can be solved analytically by induction for the first reactor (e.g., see Tadmor[17]) by introducing the following variable:

$$z_1 = K_{P,1}\tau_1[M]_1 \tag{42}$$

which equals the average number of monomer units added per initiating molecule in the first reactor. This definition is consistent with the previous definition of z for batch/plug flow reactors. The resulting MWD is a function of $z1$ only as shown below:

$$Y_{1,1} = \frac{[P_1]_1}{[P_1]_0} = \frac{[P_1]_1}{[I]_0} = \frac{1}{1 + z_1} \tag{43}$$

$$[P_x]_1 = \frac{z_1}{1 + z_1}[P_{x-1}]_1$$

$$= \left(\frac{z_1}{1 + z_1}\right)^2 [P_{x-2}]_1 = \cdots$$

$$= \left(\frac{z_1}{1 + z_1}\right)^{x-1} [P_1]_1 = \frac{z_1^{x-1}}{(1 + z_1)^x}[I]_0 \tag{44}$$

or in terms of mole fraction distribution as

$$Y_{x,1} = \frac{[P_x]_1}{[I]_0} = \frac{z_1^{x-1}}{(1 + z_1)^x} \tag{45}$$

The number-average and weight-average chain lengths, or number-average and weight-average molecular weights calculated from this distribution are

$$X_{n,1} = \frac{M_{n,1}}{F_w} = 1 + z_1 \tag{46}$$

$$X_{w,1} = \frac{M_{w,1}}{F_w} = \frac{1 + 3z_1 + 2z_1^2}{1 + z_1} = 1 + 2z_1 \tag{47}$$

The heterogeneity index (HI) is

$$HI_1 = \frac{M_{w,1}}{M_{n,1}} = \frac{1 + 3z_1 + 2z_1^2}{(1 + z_1)^2}$$

$$= 2 - \frac{1}{1 + z_1} \tag{48}$$

It can be shown from the above equation that HI converges rapidly to 2.0 at high molecular weight; e.g., 1.990 for $X_n = 100$ and 1.999 for $X_n = 1000$. For all practical purposes, HI can be considered to be 2.0 for an ideal CSTR reactor in which initiation and termination effects are negligible and where the average number chain length of the polymer is much larger than 100.

Equations (38) and (39) for the second reactor can be solved using the solution of the first reactor, those for the third reactor can be solved using the solution of the second reactor, and so forth. The solutions are similar in form to those of the first reactor except the algebra becomes increasingly complicated. The results for j-th reactor are

$$\frac{[P_x]_j}{[I]_0} = \sum_{n=1}^{j} \frac{z_n^{j+x-2}}{(1 + z_n)^x \prod_{\substack{m=1 \\ m \neq n}}^{j} (z_n - z_m)} \tag{49}$$

where z_n is defined as

$$z_n = K_{P,n} \tau_n [M]_n \tag{50}$$

which equals the average number of monomer units added per initiating molecule in the n-th reactor.

The number-average and weight-average chain lengths, or number-average and weight-average molecular weights calculated from this distribution for the j-th reactor are

$$X_{n,j} = \frac{M_{n,j}}{F_w} = 1 + G \tag{51}$$

$$X_{w,j} = \frac{M_{w,j}}{F_w} = \frac{1 + 3G + G^2 + H}{1 + G} \tag{52}$$

where G and H are defined as:

$$G = \sum_{n=1}^{j} z_n \tag{53}$$

$$H = \sum_{n=1}^{j} z_n^2 \tag{54}$$

The heterogeneity index for the j-th reactor is

$$\text{HI}_j = \frac{X_{w,j}}{X_{n,j}} = \frac{1 + 3G + G^2 + H}{(1 + G)^2} \tag{55}$$

EXPERIMENTAL

Equipment

The polymerizations were carried out in one-gallon jacketed stirred reactors in the Polymerization Reaction Engineering Lab at Goodyear Research. The reactors are run in the batch mode to obtain kinetic data and as a series of continuous reactors to confirm the combined reactor model. The high level of automation and computer control afforded by this facility enables a precise control of flow rates and temperatures; on the order of 2% and 2°C, respectively.

Material Preparation

Butadiene premix (monomer premixed at 15 to 20 wt % in the solvent) was purified by passing it through a drying column packed with 3 Å molecular sieve and silica gel. The typical premix contained a scavenge level of about 5 ppm (water equivalent).

Concentrated n-butyl lithium and TMEDA were kept refrigerated and under a nitrogen blanket until used. Dilutions to concentrations required for proper metering were made for each set of runs using high-performance liquid chromatography (HPLC) quality hexane sparged with nitrogen and stored over 3 Å mole sieves.

Rosin acid and methanol were added as shortstops (SS) and 2,6-dibutyl-$para$-cresol added as an antioxidant (AO) to the live cement at one part per hundred rubber (1 phr) each. A mixed solution of 20 wt % of each in hexane was utilized for all batch and continuous runs.

Procedure

To obtain kinetic data, polymerizations were carried out batchwise in one-gallon CSTR reactors. Prior to each run, the reactor was washed twice with polymerization grade hexane and then pickled with a solution consisting of 10 mL 1.6M n-BuLi and 2.5 kg hexane. The reactor was then evacuated and 2.0 to 2.5 kg premix charged. A sample was taken from a dip-leg and analyzed for monomer concentration by gas chromatography. Then, the required amount of TMEDA was injected into the reactor through the injection port and the reactor was brought to the desired temperature. A small amount of dilute n-BuLi was added into the reactor to scavenge the impurities in the reactor. The scavenge procedure was repeated until polymerization was detected (1) using a qualitative "foaming" technique in which bubbles remain after shaking a small vial of the reactor premix due to the increase in viscosity, and (2) monitoring precisely the drop in pressure as the reaction initiates due to monomer consumption. These techniques are able to distinguish conversions at as little as 1% of the monomer. The required amount of

initiator was injected into the reactor to start the polymerization. Errors in the determination of kinetic rate which would be due to uncertainties in the scavenging procedure were minimized by calculating the active initiator concentration from the GPC analysis of molecular weight.

To test the combined reactor model, polymerizations were carried out in the continuous mode with one-gallon CSTR reactors arranged in series. The butadiene premix was purified as before. Prior to each continuous run, a batch run was conducted to determine the premix scavenge level using the techniques described. Polymerizations were carried out until steady state was reached, again following conversion by GC. Generally this required 3–4 residence times for the first reactor and 5–6 residence times for the second reactor. The live polymer cement was terminated by the SS/AO solution in a separate vessel.

TABLE II
Operating Conditions and Polymer Structures

Temp (°C)	Modifier ratio	$[M]_0$ (mol/L)	$[I]_0$ (mmol/L)	M_n (g/mol)	HI (M_w/M_n)	Vinyl (%)
Unmodified series						
50	0.00	2.197	0.9056	122,000	1.13	8.0
50	0.00	1.898	0.3760	273,000	1.13	7.0
50	0.00	1.975	0.3102	343,000	1.16	9.0
60	0.00	1.944	0.7318	141,000	1.1	8.0
60	0.00	1.187	0.2924	349,000	1.15	8.0
60	0.00	1.834	0.2200	448,000	1.30	8.0
70	0.00	1.186	0.4007	159,000	2.17	7.0
70	0.00	1.212	0.1905	371,000	1.94	6.0
70	0.00	1.105	0.1615	370,000	1.84	6.0
Fully modified series						
10	2.50	2.290	0.8427	147,000	1.04	83.0
20	2.50	2.394	0.7846	173,000	1.05	82.0
30	2.50	2.366	0.7230	177,000	1.05	80.2
40	2.50	1.911	0.8918	116,000	1.08	77.0
40	2.50	1.786	0.3404	283,000	1.08	78.0
40	2.50	1.787	0.3239	303,000	1.11	75.0
50	2.50	1.900	0.6955	150,000	1.08	72.0
50	2.50	1.827	0.3862	263,000	1.12	72.8
50	2.50	1.977	0.2526	427,000	1.33	72.0
60	2.50	1.284	0.7063	99,800	1.10	67.0
60	2.50	1.759	0.4318	265,000	1.11	63.0
60	2.50	1.894	0.3874	266,000	1.12	67.9
Varied modification						
50	0.00	1.898	0.3760	273,000	1.13	7.0
50	0.25	2.078	0.5094	224,000	1.13	37.5
50	0.50	2.037	0.4735	236,000	1.13	53.5
50	0.75	2.083	0.5499	208,000	1.12	63.3
50	1.00	2.115	0.3784	307,000	1.03	73.9
50	1.50	1.933	0.4478	237,000	1.11	72.9
50	2.00	2.018	0.4716	235,000	1.07	74.7
50	2.50	1.827	0.3862	263,000	1.12	72.8
50	3.00	1.979	0.5150	211,000	1.08	75.2
50	3.50	2.275	0.5801	214,000	1.19	75.0

For both batch and continuous runs, monomer conversion was determined during the course of polymerization by monitoring the drop in residual monomer content in the premix. Very small samples of cement were withdrawn at increments as short as 5 minutes and coagulated in vials containing ethyl alcohol. The remaining liquor was analyzed on a robotized capillary GC. Conversions thus obtained were found to be reproducible within 1%. The polymer cements obtained were oven dried and samples sent for various analyses including glass transition (T_g) by differential scanning calorimetry (DSC), Mooney viscosity, molecular weight distribution (by GPC), and microstructures by Fourier transform infrared spectrometry (FTIR).

Design of Experiments

To establish the temperature and concentration sensitivities of the discrete species, varied levels of initiator (roughly, 100 to 400 thousand Mn equivalent) at three levels of temperature (40, 50, and 60°C) were tested in studies at both unmodified (no TMEDA) and fully modified (excess TMEDA at 2.5 TMEDA/Li) conditions (Table II). Eight polymerizations at modifier ratios between 0.25 and 3.5 gave information on the incremental effects of the modifier. Three low temperature (10–30°C) fully modified polymerizations were conducted to aid in the microstructure descriptions in this sensitive region. Data from 21 of the 29 batches were used to generate the model; the remaining eight were used to confirm the fit.

Figures 1 and 2 give typical conversion data obtained for a family of temperatures and modifier ratios, respectively. The operating conditions and polymer structures of all batch runs are shown in Table II.

Eight continuous polymerizations, most often utilizing two reactors in series, were conducted to test the combined reactor model. Operating conditions were selected to cover a broad range; data and polymer properties from each reactor were obtained.
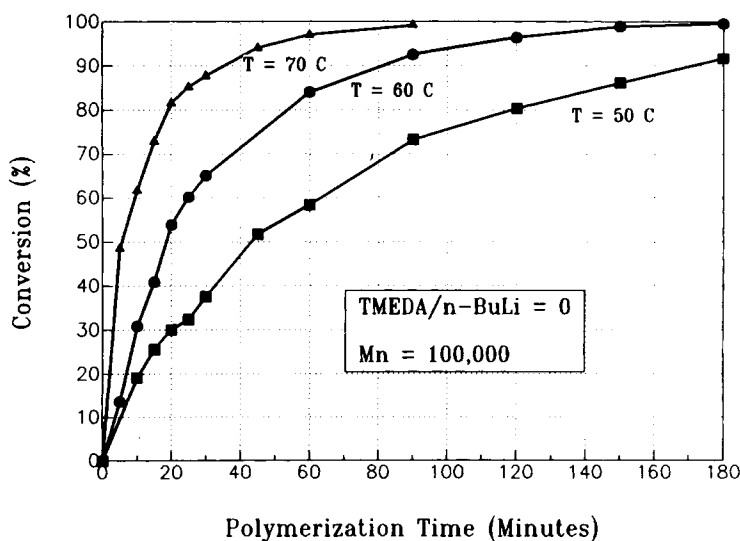

Polymerization Time (Minutes)

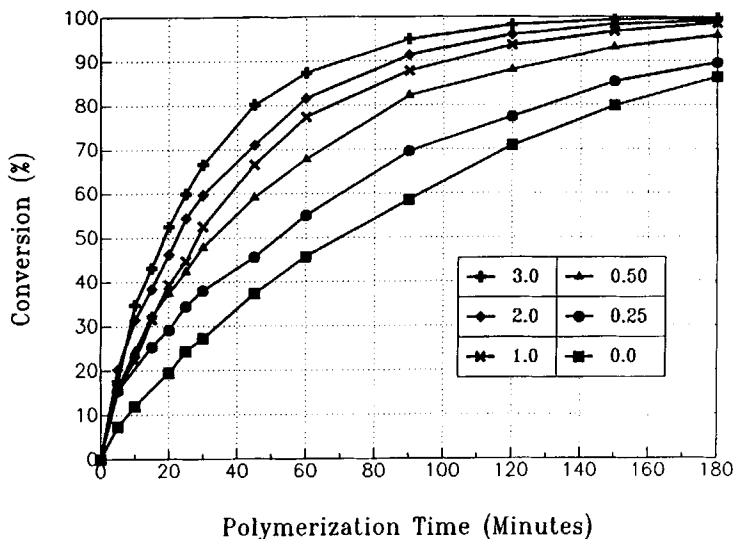Fig. 1.   Typical conversion data of unmodified PBD batch runs.

Fig. 2. Typical conversion data of modified PBD batch runs. Temperature = 50°C, M_n = 200,000. Parameter is modifier ratio.

RESULTS AND DISCUSSION

Kinetic Data Regression

Each batch kinetic run was conducted under isothermal conditions and with constant initiator concentration. K_P and $[I]_0$ were constant and, thus, eq. (22) can be used with the experimental conversion data to regress the constant $K_P[I]_0$.

For fully modified polymerization:

$$K_p[I]_0 = K_{pm}[I]_0$$

$$= K_{m0}e^{-E_m/RT}[I]_0 \qquad (56)$$

and for unmodified polymerization:

$$K_p[I]_0 = K_{pu}h[I]_0 = K_{pu}(aK_a)^{-1/a}[I]_0^{1/a}$$

$$= K_{u0}e^{-E_u/RT}[I]_0^{1/a} \qquad (57)$$

where K_{m0} and E_m are the frequency factor and activation energy of the fully modified propagation rate constant K_{pm}; K_{u0} and E_u are for the combined unmodified propagation rate constant K_{pu} and association equilibrium constant K_a; R is the gas law constant in cal/(mol-K) ($R = 1.987$); T is the reacting temperature in K; and $[I]_0$ is the effective concentration of n-BuLi in kmol/m^3 or mol/L. The obtained constant $K_P[I]_0$ can again be regressed with temperature T and initiator concentration $[I]_0$, the results are shown in Table I and summarized below.

For fully modified polymerization

$$K_p[I]_0 = 7.024 \times 10^8 e^{-10332/RT}[I]_0 \tag{58}$$

and for unmodified polymerization

$$K_p[I]_0 = 1.994 \times 10^{12} e^{-19306/RT}[I]_0^{0.3338} \tag{59}$$

The confidence factor for the modified and unmodified kinetic expressions were determined to be 0.98 and 0.96, respectively. The association constant ($a = 1/0.3338$) is 2.996 for the unmodified system indicating that the "effective" or "average" associated living polymers is almost exactly 3. It does not imply that living polymers exist as trimers. The regressed association constant for fully modified polymerization was 0.933. Since the association constant can not be less than one, the regression was repeated with the constant forced to one.

Effect of Modifier Ratio and Temperature

The effect of modifier ratio, MR = [TMEDA]/[I]$_0$, on the rate constant K_P is shown in Figure 3. It can be seen that the rate increases with increasing modifier ratio (MR) and approaches a maximum value when the modifier ratio is around 1.0. This is because associated living polymers were broken up by the TMEDA, formed a complex, and underwent faster modified polymerization. As more TMEDA was added, more associated polymers were dissociated and the rate of polymerization increased. Finally, all associated polymers were broken up when the amount of TMEDA reached the critical value (~ 1.0 MR); the reaction rate was at the maximum value and changed very little afterward. Gradual increases achieved beyond this level are attributed to
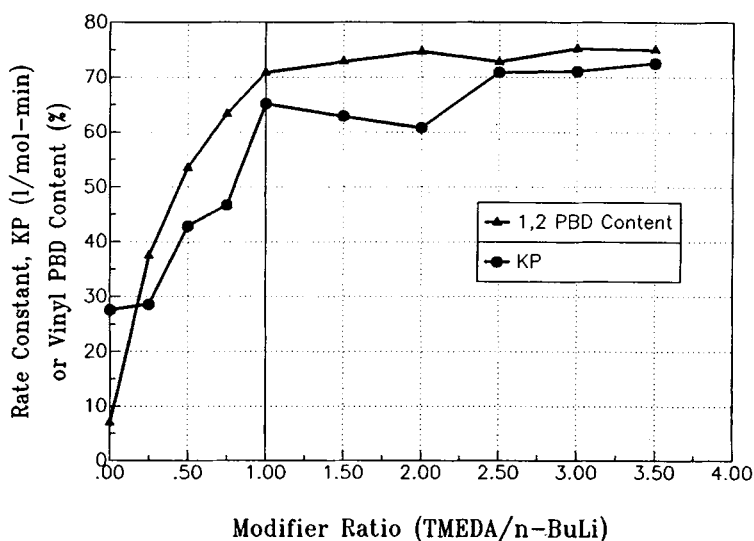

Fig. 3.   Effect of modifier ratio on rate constant and vinyl PBD content. Temperature = 50°C.

solvent effects of the modifier itself. Note also that K_P varies linearly between modifier ratio of 0 and 1.0.

Based on this information and the effect of modifier on the polymer structure to be discussed in the next section, we propose the kinetics of partially modified PBD polymerization to be

$$K_p = fK_{pm} + (1 - f)K_{pu}h \tag{60}$$

with

$$f = 1.0 \quad \text{for} \quad \text{MR} \geq 1.0$$

$$f = \text{MR} \quad \text{for} \quad 0 \leq \text{MR} < 1.0$$

The microstructure of the polymers produced depends on the polymerization temperature and modifier ratio. The experimental microstructure data were regressed to obtain the following correlation:

$$V_m = -448.8 + 3.761T - 0.006653T^2 \tag{61}$$

$$V_u = 29.644 - 0.06667T \tag{62}$$

where V_m and V_u are the regressed weight percentages of vinyl PBD (or 1,2 PBD) of the polymers produced by the fully modified and unmodified polymerizations, respectively. These correlations will be used in the model to predict the polymer structure. Similar to rate constant, the vinyl content of the polymer increases rapidly (from 8% to above 80%) with increasing modifier ratio and approaches a maximum value when the modifier ratio is around 1.0 as also shown in Figure 3. Therefore, equations of combined vinyl PBD content (vinyl), similar to those governing the combined rate constant (K_P), will be used in the model for partially modified polymerization as shown below:

$$\text{Vinyl} = \frac{fK_{pm}V_m + (1 - f)K_{pu}hV_u}{K_p} \tag{63}$$

with

$$f = 1.0 \quad \text{for} \quad \text{MR} \geq 1.0$$

$$f = \text{MR} \quad \text{for} \quad 0 \leq \text{MR} < 1.0$$

Slight changes in modifier ratio, resulting from normal variations during manufacturing in impurity levels and flow rate will result in relatively large changes in the vinyl content and the glass transition temperature of the polymer. Above 1.0, the sensitivity of the microstructure and production rates are greatly reduced, and operating in this region is preferred for process and product control. Vinyl content in this region is primarily through temperature control.

To examine the degree of model fit, experimentally obtained kinetic rate constants, conversions, and microstructure were plotted against values deter-
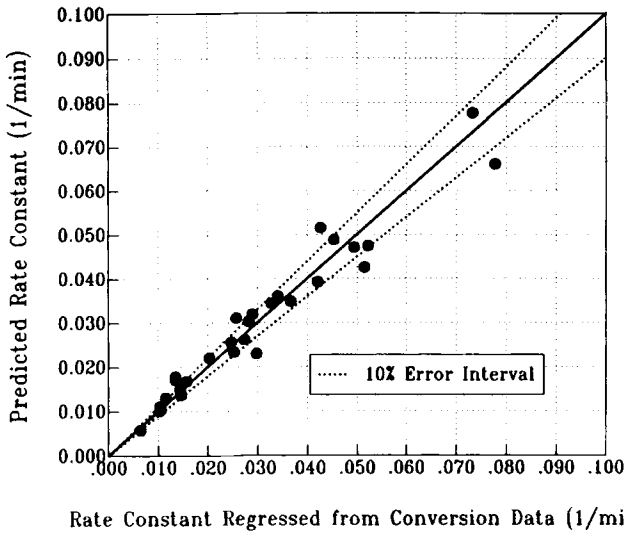
Fig. 4. Comparison between predicted and regressed first order rate constant (KP*IO).

mined by the model. The kinetic rates of all of the batch runs including partially modified runs where $0 < MR < 1$ are plotted in Figure 4. Generally, the rate constants are composition sensitive (both initiator and monomer) and are expected to vary around the average, upon which the model is based; the majority are seen to fall within the $\pm 10\%$ envelope.

Results for Continuous Polymerization

The conversion and heterogeneity indices were predicted using the CSTR reactor model described in eqs. (41) and (55). The value for K_P was calculated
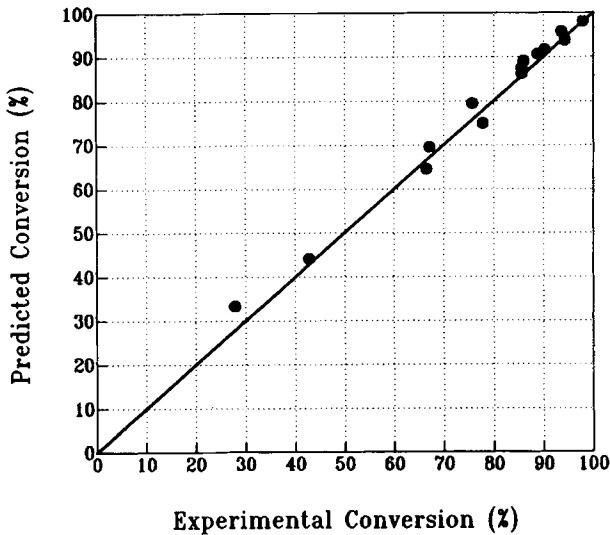
Fig. 5. Comparison between predicted and experimental conversions: 2 CSTR Reactor System.
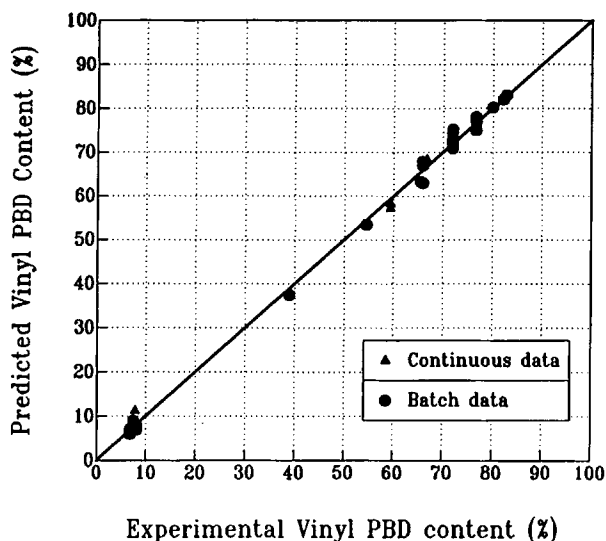
Fig. 6. Comparison between predicted and experimental vinyl PBD content.

from eqs. (58) and (59), the regressed batch kinetic equations for modified and unmodified polymerizations. The K_P for modifier ratio between 0 and 1 was calculated using eq. (60). The vinyl contents were determined from eqs. (61), (62), and (63) in a similar manner. The results for actual continuous runs were compared with the model predictions.

The predicted and experimental conversions of the continuous runs are plotted in Figure 5; the average difference is 2.0% (absolute) or 3.9% (relative). The predicted and experimental vinyl content of continuous runs, and partially modified batch runs which were not used to regress the model, are plotted in Figure 6. The average difference is 1.5% vinyl content.
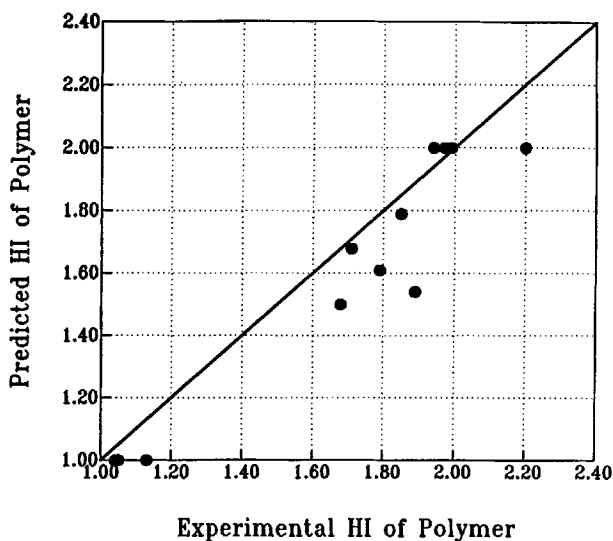

Fig. 7. Comparison between predicted and experimental HI of polymers.

The heterogeneity index (HI) is a function of the average number of monomer units added or, equivalently, the conversion in each reactor. The calculated value was based on the assumption that there was no termination reaction involved. If the living polymer chains were terminated, actual HI would be greater than the calculated ideal value. As can be seen in Figure 7, some indication of termination, particularly at higher temperatures, is evident and can be added to the model. Even so, the average difference between the calculated and experimental heterogeneity index is 0.14 (or 7.1% relative error).

Process Simulation

The conversions, molecular weight distributions, and microstructure for any combination of reactor system and operating condition can be calculated using the fundamental models developed. As an example, a chain of multiple, equal volume CSTR reactors has been simulated. Combinations of CSTR and plug flow reactors, and chains of unequal size CSTRs, may just as easily be solved.

The effect of reactor residence time on conversion for chains of one, two, and three reactors, operated at a fixed set of conditions, is shown in Figure 8. As expected, the conversion increases with increasing reactor residence time (as well as with temperature, initiator level and modifier ratio, within limits). Multiple series CSTRs yield a higher conversion than a single CSTR with the same total residence time. Maximum conversion is obtained with an infinite number of reactors; emulating a plug flow or batch reactor. Higher capital costs of multiple reactor chains may be offset by the reduced operating costs derived from higher conversion and reduced recycle requirements. Higher conversion polymers will also be less prone to molecular weight variations resulting from process perturbations. The distributions of residence time and
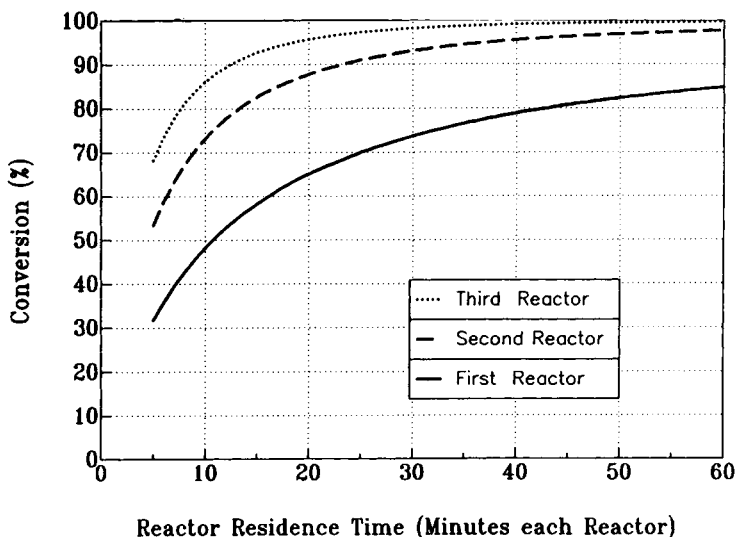

Fig. 8. Effect of reactor residence time on conversion of modified polymerization in a 3-CSTR reactor chain (RT1 = RT2 = RT3). Temperature = 70°C. Target M_n = 250,000.
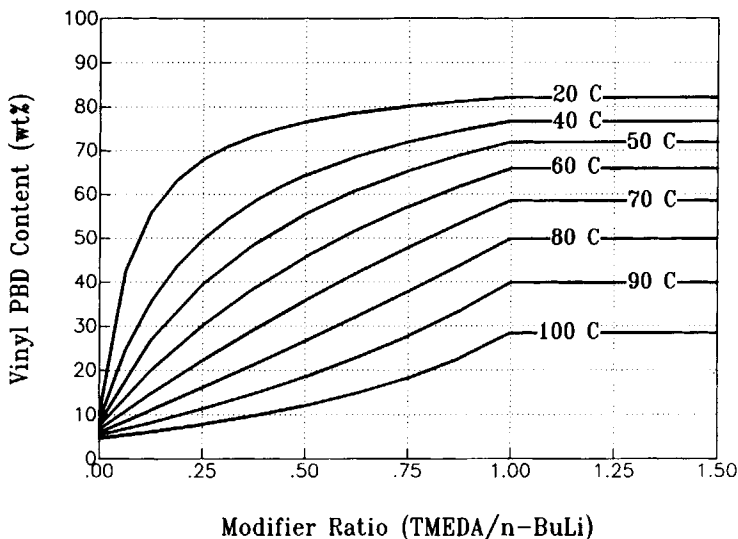
Fig. 9. Effects of modifier ratio and temperature on vinyl PBD content.

molecular weight will need to be considered when selecting among possible reactor systems.

For unmodified (and highly associated) polymerization, as the conversion increases, the cement becomes extremely viscous. In very viscous fluids, the overall reaction rate might be expected to decrease due to the additional mass transfer resistance. As the actual conversions were accurately predicted for the range of conditions encountered, the effect of viscosity was not considered in the model.

The effect of temperature and modifier ratio on microstructure is shown in Figure 9. As is well known, the vinyl content increases with decreasing polymerization temperature and increasing modifier ratio. Of importance is the nature of the specific curves for the family of temperatures. At low temperatures, vinyl content increases rapidly with even a modest increase in modifier ratio, giving a convex curve. At high temperatures, the increase is delayed until high levels of modification are achieved, giving a concave curve. The explanation is evident from the kinetic model.

The increase in the rate of polymerization of the modified species with temperature is given by eq. (58). The increase in the rate of polymerization of the unmodified species with temperature takes into account the increased number of active chains resulting from the shift in association equilibrium toward the dissociated state, and is given by eq. (59). The unmodified reaction is shown to be slower than the modified reaction at low temperatures, approximately equal at 70°C, and actually faster at higher temperatures. The microstructure of the resulting product is a combination of the contributions of the respective reactions, with unmodified species yielding primarily 1,4 microstructures and modified species yielding primarily 1,2 microstructure. At the lower temperatures, a small amount of modified initiator will contribute a disproportionately large amount of polymer having a primarily 1,2 microstruc-
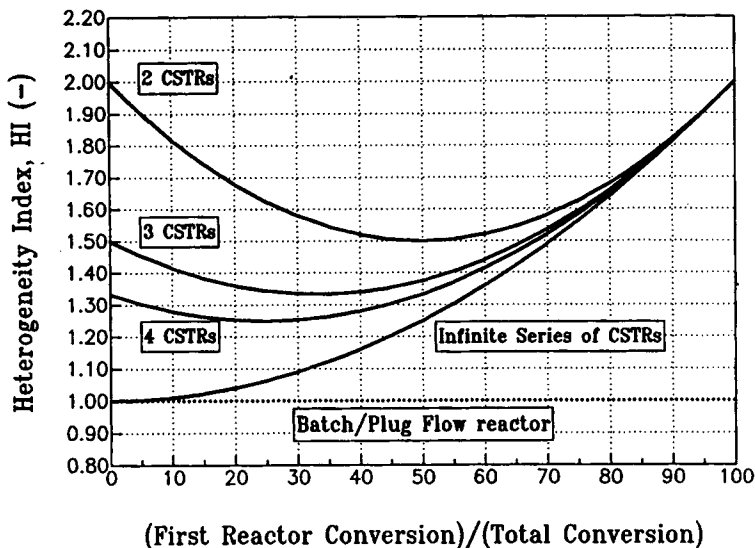
Fig. 10. Heterogeneity index for CSTR reactor chains. Effect of first reactor conversion, other reactor conversions equal.

ture. At higher temperatures, modified initiator will not react as fast as the unmodified, but dissociated, species and the product will retain a predominantly 1,4 microstructure until high levels of modification are achieved. The curve at 70°C shows a nearly linear relationship between microstructure and modifier level, reflecting equivalent rates and contributions.

The number-average molecular weight of the polymer is calculated by dividing the weight of monomer reacted by the effective amount (in moles) of initiator, without regard to the reactor configuration and operating conditions. The molecular weight distribution of polymer, on the other hand, depends on the reactor configuration and the resulting residence time distribution, as well as on any initiation and termination effects. The polymer molecular weight distribution, represented by the heterogeneity index (HI = M_w/M_n), is a function of the number of monomer units added per initiating molecule in each reactor as shown in eq. (55) or, equivalently, the conversion in each reactor (Fig. 10). For polymerization carried out in an ideal batch or plug flow reactor, the heterogeneity index has been shown to be 1.0, while for an ideal CSTR reactor it is 2.0.[16,17]

In the absence of strong initiation and termination effects, the HI for any particular process will fall between these two limits. The envelope of minimum possible heterogeneity index for chains of CSTRs can be calculated (Fig. 10) as a function of conversion in any one of the reactors. The maximum (HI = 2.0) occurs when one reactor in the chain contributes essentially all of the production (conversion). The minimum HI occurs when all of the N reactors contribute equally, whereby: HI = 1 + 1/N. In reality, the actual heterogeneity index will be higher as a finite amount of time is required for initiation, and some termination will occur due to impurities and/or thermolysis.

CONCLUSIONS

The TMEDA/n-BuLi ratio has a dramatic effect on the anionic polymerization of polybutadiene. Typically, polymerizations of these types are described for either fully modified or unmodified systems. Equations (58) and (59) describe the regressed propagation kinetic constants for these two cases as determined from batch kinetic data for a wide range of operating conditions. Both equations are based on the classic assumptions for solving polymerization kinetic expressions including instantaneous initiation and no termination for this particular system.

It is assumed that unmodified polymerization is affected by strong association of the living anionic polymer species and that only the dissociated species react. This model provides on quantitative explanation of the kinetic order of the initiator concentration in the rate expression. The data are internally consistent with a high degree of fit demonstrated.

Since the propagation constant varies linearly with the modifier ratio, we proposed competing, parallel reactions involving modified and unmodified species. Hence, the kinetic propagation constant for the partially modified case can be described by eq. (60). This lumped propagation constant substituted into the appropriate reactor model (batch, CSTR) compares favorably to actual data for rate constants, conversion, and polymer vinyl content for both batch and 1 or 2 CSTR operations.

The conversion, molecular weight distribution, and microstructure for various combinations of reactor system and operating conditions have been successfully calculated. Simulations of these types can be used to design reactor systems, predict polymer properties of a large-scale operation from results of small-scale batch reactor runs, and explain results on a fundamental basis.

References

1. R. N. Young, R. P. Quirk, and L. J. Fetters, in *Advances in Polymer Science*, Vol. 53, Springer-Verlag, Berlin-Heidelberg-New York, 1984.

2. M. Van Beylen, S. Bywater, G. Smets, M. Szwarc, and D. J. Worsfold, in *Advance in Polymer Science*, Vol. 86, Springer-Verlag, Berlin-Heidelberg-New York, 1988.

3. M. Morton, L. J. Fetters, and E. E. Bostick, *J. Polym. Sci. C*, 1, 311 (1963).

4. M. Morton, E. E. Bostick, and L. J. Fetters, *J. Polym. Sci. A*, 1, 1735 (1963).

5. M. Morton and L. J. Fetters, *J. Polym. Sci. A*, 2, 3311 (1964).

6. M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, New York, 1983.

7. J. N. Hay, J. F. McCabe, and J. C. Robb, *J. Chem. Soc., Faraday Trans.*, 1, 68 (Pt. 1), 1 (1972).

8. A. F. Johnson and D. J. Worsfold, *J. Polym. Sci. A*, 3, 449 (1965).

9. H. L. Hsieh, *J. Polym. Sci. A*, 3, 153 (1965).

10. H. L. Hsieh, *J. Polym. Sci. A*, 3, 163 (1965).

11. H. L. Hsieh, *J. Polym. Sci. A*, 3, 173 (1965).

12. H. L. Hsieh and W. H. Glaze, *Rubber Chem. Technol.*, 43 (1), 22 (1970).

13. V. P. Shatalov, I. Yu. Kirchevskaya, A. R. Samotsvetov, and N. P. Proskurina, *Polym. Sci. USSR* (Engl. Transl.), 15, 2309 (1973).

14. D. J. Worsfold and S. Bywater, *Macromolecules*, **5**, 393 (1972).

15. W. H. Glaze, J. E. Hanicak, M. L. Moore, and J. Chaudhuri, *J. Organomet. Chem.*, **44**, 39 (1972).

16. P. J. Flory, *Principle of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.

17. Z. Tadmor, "The Influence of Reactor Dynamics on Molecular Weight Distributions In Batch and Continuous Polymerizations," Ph.D. dissertation, Stevens Institute of Technology, Hoboken, NJ, 1966.

18. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.